

PATENT COOPERATION TREATY

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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

Date of mailing (day/month/year) 07 February 2001 (07.02.01)	
International application No. PCT/US00/15950	Applicant's or agent's file reference WRI-Colx-PCT
International filing date (day/month/year) 09 June 2000 (09.06.00)	Priority date (day/month/year) 10 June 1999 (10.06.99)
Applicant SCHABRON, John, F. et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

13 December 2000 (13.12.00)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference WRI-COIX-PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/15950	International filing date (day/month/year) 09 June 2000 (09.06.2000)	Priority date (day/month/year) 10 June 1999 (10.06.1999)
International Patent Classification (IPC) or national classification and IPC IPC(7): GOIN 35/08, 31/00, 31/16, 33/00 and US Cl.: 436/55, 60, 139, 163		
Applicant THE UNIVERSITY OF WYOMING RESEARCH CORPORATION		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>5</u> sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of <u>10</u> sheets.</p> <p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of report with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input checked="" type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application 		
Date of submission of the demand 13 December 2000 (13.12.2000)	Date of completion of this report 28 September 2001 (28.09.2001)	
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. 703.305.3230	Authorized officer Jill A. Warden Telephone No. 703.305.3066	

Form PCT IPEA: 409 (cover sheet) July 1998

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

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I. Basis of the report

1. With regard to the elements of the international application:*

- ☐ the international application as originally filed.
- ☒ the description:
pages 1-42 as originally filed
pages NONE filed with the demand
pages NONE filed with the letter of _____.
- ☒ the claims:
pages NONE as originally filed
pages NONE as amended (together with any statement) under Article 19
pages NONE filed with the demand
pages 43-52 filed with the letter of 27 September 2001 (27.09.2001)
- ☒ the drawings:
pages 1-13 as originally filed
pages NONE filed with the demand
pages NONE filed with the letter of _____.
- ☐ the sequence listing part of the description:
pages NONE as originally filed
pages NONE filed with the demand
pages NONE filed with the letter of _____.

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language _____ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in printed form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

- ☒ the description, pages NONE
- ☒ the claims, Nos. 49-93
- ☒ the drawings, sheets/fig NONE

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.1(c) and 70.2(c)).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/15950**V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. STATEMENT**

Novelty (N)	Claims <u>1-48</u>	YES
	Claims <u>NONE</u>	NO
Inventive Step (IS)	Claims <u>15-44, 47 and 48</u>	YES
	Claims <u>1-14, 45 and 46</u>	NO
Industrial Applicability (IA)	Claims <u>1-48</u>	YES
	Claims <u>NONE</u>	NO

2. CITATIONS AND EXPLANATIONS

Claims 1-12, 45, 46 lack an inventive step under PCT Article 33(3) as being obvious over Supernaw et al. (US 4,990,773). Supernaw discloses "a method of evaluating a sample of an underground formation such as drill cuttings to determine the producibility of any hydrocarbons present in the formation by solvating a sample in a polar solvent which will solvate asphaltenes, solvating the sample in an aliphatic solvent which will solvate most crude fractions without solvating asphaltenes, quantitatively measuring the emission fluorescence at a wavelength below 400 nm of both solvated samples at an excitation wavelength at which most petroleum compounds fluoresce, and determining the producibility of any hydrocarbon present in the sample by comparing the emission fluorescence of the two samples to previous correlations made between fluorescence and known producibility" (Abstract). Supernaw further discloses that when the instant ratio is less than three, the hydrocarbons involved are most likely producible (col. 5, lines 10-15). It would have been within the skill of the routineer in the art to derive indicia of stability as they are disclosed in the instant Application, using Supernaw method, because they are based on the ratio of solvated and non-solvated asphaltenes.

Claims 13, 14 lack an inventive step under PCT Article 33(3) as being obvious over Barbour, which discloses analysis of maltenes with size exclusion chromatography.

Claims 15-44 and 47, 48 the criteria set out in PCT Article 33(2)-(4), because the prior art does not teach or fairly suggest using polystyrene as calibrating compound in analysis of maltenes, determining a concentration of asphaltenes at zero titrant level, and determining D₉₅, as recited in claim 26.

----- NEW CITATIONS -----

US 4,990,773 A (SUPERNAW et al.) 05 February 1991, see Abstract and column 5, lines 1-45;
BARBOUR et al. "Analysis of SHRP asphalt nonpolar fractions by supercritical fluid chromatography", Fuel Sci. Technol. Int., 1992, vol. 10, pages 979-1001 (Abstract)

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VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

The description is objected to as containing the following defect(s) under PCT Rule 66.2(a)(iii) in the form or contents thereof: the term "a dilution concentration" does not have any sensible meaning and is suggested to be replaced with an accepted terminology, e.g. a concentration of a specific compound at zero titrant value.

Claim 4 is objected to under PCT Rule 66.2(a)(iii) as containing the following defect(s) in the form or contents thereof: the formula for K contains a dollar sign, which does not have any meaning in this context. A multiplication sign (x) should be written instead.

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VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the questions whether the claims are fully supported by the description, are made:

Claims 1-12 are objected to as lacking clarity under PCT Rule 66.2(a)(v) because practice of the claimed invention is not adequately described in writing, as required under PCT Rule 5.1(a)(iii), for the reasons set forth in the immediately preceding paragraph.

Claims 1-12 are objected to as lacking clarity under PCT Rule 66.2(a)(v) because practice of the claimed invention is not enabled as required under PCT Rule 5.1(a) for the reasons set forth in the immediately preceding paragraph.

Claim 1 recites "a method of processing petroleum residua", however no steps of this processing are recited. The only steps, that can be considered as of process claim, are precipitation and extraction of asphaltenes. However, these steps are evidently not what was meant by the expression "a method of processing petroleum residua". This renders claim indefinite.

Claims 2-4 recite certain values of parameters K_d and K_f . However, these parameters were not defined, and therefore it is not clear, what is meant by their values.

Claim 6 recites Ω_y , however, it is not clear from the claim, what this parameter means.

VI. CLAIMS

We claim:

1. A method of processing petroleum residua, comprising the steps of:
 - a. providing an amount of said petroleum residua having solvated asphaltenes dispersed in lower polarity solvents;
 - b. determining a value for said petroleum residua at which said solvated asphaltenes fail to disperse in said lower polarity solvents further comprising the steps of:
 - i. precipitating an amount of asphaltene_x from an amount of said petroleum residua with a first solvent;
 - ii. extracting said amount of asphaltene_x with a second solvent, wherein said second solvent has a polarity between a polarity of said first solvent and a polarity of a third solvent capable of dissolving said asphaltene_x completely; and
 - iii. determining a threshold of instability value of said petroleum residua, wherein said threshold of instability value corresponds to weight percent asphaltene_y soluble in said second solvent to weight percent asphaltene_x precipitated by said first solvent below which said petroleum residua generates undispersed asphaltene_y; and
 - c. processing said petroleum residua under conditions that maintains a value of said weight percent asphaltene_y soluble in said second solvent to weight percent asphaltene_x precipitated by said first solvent above said threshold of instability value.
2. A method of processing petroleum residua as described in claim 1, wherein said step of processing said petroleum residua under conditions that maintains a value of said weight percent asphaltene_y soluble in said second solvent to weight percent asphaltene_x precipitated by said first solvent above said threshold of instability value comprises processing said petroleum residua under conditions maintaining a value for K, equal to or

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greater than 1.1.

3. A method of processing petroleum residua as described in claim 1, wherein said step of processing said petroleum residua under conditions that maintains a value of said weight percent asphaltenes, soluble in said second solvent to weight percent asphaltenes, precipitated by said first solvent above said threshold of instability value comprises processing said petroleum residua under conditions maintaining a value of K_r equal to or greater than about 1.4.

4. A method of processing petroleum residua as described in claim 1, wherein said step of processing said petroleum residua under conditions that maintains a value of said weight percent asphaltenes, soluble in said second solvent to weight percent asphaltenes, precipitated by said first solvent above said threshold of instability value comprises maintaining a solvation shell (K), wherein $K = (K_s, K_r)$ has a value equal to or greater than about 1.5.

5. A method of processing petroleum residua as described in claim 1, wherein said step of providing an amount of petroleum residua further comprises the step of selecting said petroleum residua from the group consisting of coal tars, shale oils, tar sand bitumen, asphalts, and heavy oils.

6. A method of processing petroleum residua as described in claim 2, wherein $K_s = 1/(1 - \chi_v)$.

7. A method of processing petroleum residua as described in claim 3, wherein $K_r = 1/(1 - p_d)$.

8. A method of processing petroleum residua, comprising the steps of:
a providing an amount of said petroleum residua having solvated core materials dispersed in lower polarity solvents.

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- b. determining a value for said petroleum residua at which said petroleum residue generates undispersed core materials comprising the steps of:
- i. determining the amount of electromagnetic radiation absorbed by said core materials;
 - ii. determining the amount of electromagnetic radiation absorbed by said solvated core materials;
 - iii. determining a threshold of instability value of said petroleum residua, based upon the ratio of said amount electromagnetic radiation absorbed by said core materials and said amount of electromagnetic radiation absorbed by said solvated core materials corresponding to generation of undispersed materials within said petroleum residua; and
- c. processing said petroleum residua under conditions that maintains a ratio of said amount of electromagnetic radiation absorbed by said core materials and said amount of electromagnetic radiation absorbed by said solvated core materials above said threshold of instability value.
9. A method of processing petroleum residua as described in claim 8, further comprising the step of determining a threshold of instability value of said petroleum residua, based upon the ratio of said amount electromagnetic radiation absorbed by said core materials and said amount of electromagnetic radiation absorbed by said solvated core materials corresponding to generation of undispersed materials within said petroleum residua comprises determining K_i .
10. A method of processing petroleum residua as described in claim 9, further comprising the step of, determining a value of K_p of said petroleum residua, wherein absorption of electromagnetic radiation by solvent associated with said solvated core materials and absorption of electromagnetic radiation by a plurality of solvated core materials are analyzed to determine K_p .

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11. A method of processing petroleum residua as described in claim 10, further comprising the step of determining a value of $K = K_s + K_f$ of said petroleum residua, wherein absorption of electromagnetic radiation by said solvated core material and absorption of electromagnetic radiation by said core material are analyzed to determine K_s , and wherein absorption of electromagnetic radiation by said solvent associated with said solvated core materials and absorption of electromagnetic radiation by said plurality of solvated core materials are analyzed to determine K_f .

12. A method of processing petroleum residua as described in claim 11, wherein a threshold of instability value based on K has a value of about 1.5.

13. A method of analyzing petroleum residua, comprising the steps of:

- a. providing a maltenes analysis device;
- b. calibrating said maltenes analysis device;
- c. mixing an amount of petroleum residua in a precipitating solvent;
- d. precipitating asphaltenes from said petroleum residua;
- e. extracting maltenes into said precipitating solvent;
- f. analyzing maltenes with said maltenes analysis device; and
- g. determining an amount of petroleum residua stability component in said maltenes.

14. A method of analyzing petroleum residua as described in claim 13, wherein said step of providing a maltenes analysis device comprises selecting said maltenes analysis device from the group consisting of a nuclear magnetic resonance spectroscopy device, a mass spectrometry device, an infrared spectrometry device, an infrared raman spectroscopy device, a size exclusion chromatography device, a gel electrophoresis device, and a paper chromatograph device.

15. A method of analyzing petroleum residua as described in claim 13 wherein said step

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of calibrating said hydrocarbon material component analysis device comprises identifying characteristics of polystyrene having known molecular weight.

16. A method of analyzing petroleum residua as described in claim 13, wherein said precipitating solvent comprises iso-octane.

17. A method of analyzing petroleum residua as described in claim 13, wherein said step of analyzing said maltenes with said maltenes analysis device comprises:

- a. separating said maltenes with said size exclusion chromatography device; and
- b. comparing elution volumes of said maltenes to elution volumes of said components of polystyrene having known molecular weight.

18. A method of analyzing petroleum residua as described in claim 13, wherein determining an amount of said petroleum residua stability component in said maltenes comprises detecting an apparent molecular weight of said petroleum residua stability component.

19. A method of analyzing petroleum residua as described in claim 18, wherein detecting the apparent molecular weight of said petroleum residua stability component comprises observing elution of said petroleum residua stability component corresponding to a leading edge high molecular weight shoulder component.

20. A method of analyzing petroleum residua as described in claim 19, wherein said leading edge high molecular weight component has an apparent molecular weight about equal to or greater than about 500 Dalton.

21. A method of analyzing petroleum residua comprising the steps of:

- a. providing a titration device;
- b. mixing an amount of said petroleum residua into an amount of aromatic solvent (V_1).

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- c. titrating aromatic solvent soluble components in said amount of aromatic solvent with an amount of weak aliphatic solvent until a flocculent forms (V_f);
- d. calculating the flocculation ratio at infinite dilution (FR_{max}), wherein $FR_{max} = V_f / (V_f + V_w)$, and wherein V_f has a value about equal to said volume of aromatic solvent, and wherein V_w has a value about equal to said amount of weak solvent;
- e. determining the dilution concentration at zero titrant level (C_{min}), wherein $C_{min} = W_r / (V_f + V_w)$, and wherein W_r has a value about equal to said amount of said petroleum residua;
- f. determining the peptizability of asphaltenes determining (p_a), wherein $p_a = 1 - FR_{max}$; and
- g. determining a value of p_a / C_{min} .

22. A method of analyzing petroleum residua as described in claim 21, wherein said step of mixing an amount of said petroleum residua into an amount of aromatic solvent (V_f) comprises mixing said amount of said petroleum residua into an amount of toluene.

23. A method of processing hydrocarbon material as described in claim 21, wherein said step of titrating aromatic solvent soluble components in said volume of aromatic solvent with an amount of weak aliphatic solvent until a flocculent forms (V_f) comprises titrating said aromatic solvent soluble components in said volume of aromatic solvent with an amount of iso-octane.

24. A method of analyzing petroleum residua as described in claim 21, further comprising the step of comparing said value of p_a / C_{min} for an amount of toluene soluble components to a threshold of instability p_a / C_{min} having a value within the range of about 0.1 to about 0.4 .

25. A method of processing petroleum residua as described in claims 1, 8, 13, or 21 further comprising the step of predicting the proximity of said hydrocarbon material to coke

formation.

26. A method of processing petroleum residua, comprising the steps of:
- providing a titration device;
 - mixing an amount of said petroleum residua into an amount of aromatic solvent (V_a);
 - titrating aromatic solvent soluble components in said amount of aromatic solvent with an amount of weak aliphatic solvent until a flocculent forms (V_f);
 - calculating the flocculation ratio at infinite dilution (FR_{max}), wherein $FR_{max} = V_a / (V_a + V_f)$, and wherein V_a has a value about equal to said amount of aromatic solvent, and wherein V_f has a value about equal to said amount of weak aliphatic solvent;
 - determining the peptizability of asphaltenes p_a , wherein $p_a = 1 - FR$;
 - precipitating an amount of asphaltenes from an amount of said petroleum residua with a precipitating solvent;
 - determining the mass fraction asphaltenes (χ_a);
 - determining ϕ_{rs} , wherein $\phi_{rs} = 1 - K_a (1/1 - p_a) (\chi_a/1.2)$;
 - determining a threshold of instability value of said petroleum residua, wherein said threshold of instability corresponds to a value of ϕ_{rs} below which said petroleum residua generates undispersed core materials; and
 - processing said petroleum residua under conditions that maintains a value of ϕ_{rs} above said threshold of instability value.

27. A method of processing petroleum residua as described in claim 26, wherein said step of mixing an amount of said petroleum residua into an amount of aromatic solvent (V_a) further comprises selecting said aromatic solvent from the group consisting of toluene, benzene, xylene, and ethylbenzene.

28. A method of processing petroleum residua as described in claim 26, wherein said step of titrating aromatic solvent soluble components in said amount of aromatic solvent with an amount of weak aliphatic solvent until a flocculent forms (V_f) further comprises selecting said aliphatic solvent from the group consisting of iso-octane, pentane, hexane, and

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hexadecane.

29. A method of processing petroleum residua as described in claim 26, wherein said step of precipitating an amount of asphaltenes from an amount of said petroleum residua with a precipitating solvent further comprises the step of selecting said precipitating solvent from the group consisting of iso-octane, pentane, hexane, and heptane.

30. A method of processing petroleum residua as described in claim 26, further comprising the step of determining an initial amount of coke formation when exceeding said threshold of instability value.

31. A method of processing petroleum residua as described in claims 1, 8, 13, 21, or 26, further comprising the steps of:

- a. selecting distillation parameters of said petroleum residua to avoid reaching said threshold of instability;
- b. distilling said petroleum residua using said distillation parameters; and
- c. avoiding said threshold of instability.

32. A method of processing petroleum residua as described in claim 31, wherein said step of selecting distillation parameters avoid reaching said threshold of instability comprises selecting distillation parameters to avoid coke formation.

33. A method of processing petroleum residua as described in claims 31, further comprising the step of maintaining continuous distillation of petroleum residua.

34. A method of processing petroleum residua as described in claim 31, wherein said step of distilling said petroleum residua using said distillation parameters comprises the step of distilling said petroleum residua to closer proximity of said threshold of instability compared to typical distillation parameters

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35. A method of processing hydrocarbon material as described in claims 1, 8, 13, 21, or 26, further comprising the steps of:
- a. selecting distillation parameters for said petroleum residual to reach a predetermined level of stability;
 - b. distilling said petroleum residua using said distillation parameters; and
 - c. continuing distillation of said petroleum residua until reaching said predetermined level of stability.
36. A method of processing hydrocarbon material as described in claim 35, wherein said step of reaching said predetermined level of instability comprises initiating formation of a predetermined amount of coke.
37. A method of processing hydrocarbon material as described in claim 35, further comprising the step of maintaining continuous distillation until reaching said predetermined level of stability.
38. A method of processing hydrocarbon material as described in claim 35, further comprising the step of determining the hydrogen-carbon ratio of said petroleum residua.
39. A method of processing hydrocarbon material as described in claim 38, further comprising the step of determining a total amount of coke which may form from said petroleum residua.
40. A method of processing hydrocarbon material as described in claim 35, further comprising the step of increasing output of liquid distillate per unit amount of said petroleum residua.
41. A method of processing hydrocarbon material as described in claim 35, further comprising the step of decreasing the amount of energy used per unit of liquid distillate

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produced.

42. A method of processing hydrocarbon material as described in claim 35, further comprising the step of reducing the amount of emissions generated per unit of liquid distillate produced.

43. A method of processing hydrocarbon material as described in claim 42, wherein said step of reducing the amount of emissions generated per unit of liquid distillate produced comprises reducing carbon dioxide emissions.

44. A method of processing hydrocarbon material as described in claim 35, further comprising the step of increasing the purity of at least a portion of said liquid distillates.

45. Liquid distillate produced in accordance with the process of claim 1.

46. Liquid distillate produced in accordance with the process of claim 8.

47. Liquid distillate produced in accordance with the process of claim 21.

48. Liquid distillate produced in accordance with the process of claim 26.

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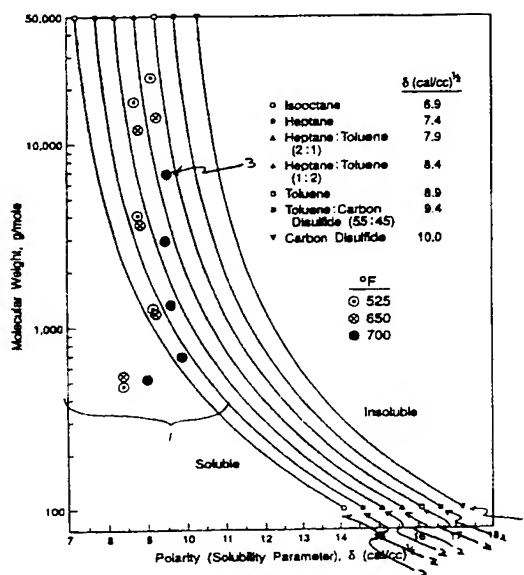
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[Continued on next page]

(54) Title: PREDICTING PROXIMITY TO COKE FORMATION



(57) Abstract: A molecular weight - polarity map having solvent-tuned contour lines (2) defining a core material solubility region (1) within which molecular weight - polarity coordinate locations (3) for components of hydrocarbon materials reside. Unimodal characteristics provide ascertainable indicators of stability or thresholds of instability used to assess the proximity of the unimodal characteristics associated with hydrocarbon materials to formation of multimodal characteristics. The invention may be used to evaluate suitability of such hydrocarbon materials to various types of processing methodologies, or to determine processing parameters, either prior to processing or during processing. Prediction of proximity to formation of multimodal characteristics may result in continuous process parameters, or increased output, decreased energy use or decreased amount of emissions per unit of such hydrocarbon materials compared to conventional processing technology. Unimodal products produced or unimodal products processed with this technology may also have a higher level of purity.

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patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— *Without international search report and to be republished upon receipt of that report.*

PREDICTING PROXIMITY TO COKE FORMATION

I. TECHNICAL FIELD

Generally, methods and apparatus for evaluating or processing hydrocarbon materials having unimodal characteristics which may acquire multimodal characteristics upon processing. Specifically, indicators of stability for hydrocarbons having unimodal characteristics which may be used separately, or used in combination, or used in comparison to a determined threshold of instability for such unimodal characteristics, to assist in determining the proximity of hydrocarbon materials having unimodal characteristics to formation of multimodal characteristics, or to assist in pre-determining the degree of acquired multimodal characteristics in response to various processing parameters.

II. BACKGROUND

It can be difficult to evaluate, in response to a given set of processing parameters, if, or when, or to what degree, a hydrocarbon material of homogeneous mixture may transition to a hydrocarbon material of heterogeneous mixture to form carbon rich materials, such as coke. When hydrocarbon materials, such as heavy oils, petroleum residua, shale oils, coal tars, tar sand bitumen, asphalts, or the like, are processed at non-pyrolytic temperatures (at or below 340°C or 644 °F), or are heated above the temperature at which pyrolysis occurs (at about 340°C or 644 °F), there is typically an induction period before deposition of carbon rich materials occurs. This induction period can be variable, ranging from a few seconds to hours, depending on the particular hydrocarbon material and the temperature at which it is processed. To avoid deposition of carbon rich material, refiners often process hydrocarbon materials based on arbitrary criteria. Because arbitrary criteria are used, conventional processing of hydrocarbon materials can result in product yields that may not be maximal.

Because of the substantial benefits that can result from predicting if, when, or to what degree particular processing parameters may induce hydrocarbon materials to form heterogeneous mixtures, there has been extensive commercial interest in technology to define indicators of stability with respect to the homogeneous mixture, or to define thresholds of instability at which transition to the heterogeneous mixture may occur. Such

indicia of stability or thresholds of instability for hydrocarbon materials may be used, for example, to evaluate the suitability of hydrocarbon materials for particular types of processing, to predict the proximity to carbon deposition or coke formation, or for controlling hydrocarbon material processing in a manner which eliminates, minimizes, or
5 predicts the amount of carbon deposition or coke formation. Even though commercial interest has generated substantial research in various fields, a long felt but unresolved need remains for methods of determining when hydrocarbon materials comprise homogeneous mixtures, or for development of indicia of stability for such homogeneous mixtures, or for more objective thresholds of instability for such homogeneous mixtures to
10 assist in predicting proximity to formation of heterogeneous mixtures. See for example, United States Patent No. 5,853,565, hereby incorporated by reference. As such, substantial problems with respect to the evaluation of hydrocarbon materials for processing, or to the processing of hydrocarbon materials, remained unresolved.

A significant problem with conventional technology for the evaluation and
15 processing of hydrocarbon material may be the failure of conventional technology to define, provide measures for, or interpretations of, the dynamics of unimodal characteristics of intact hydrocarbon materials. Unimodal characteristics define a comprehensible pattern of attributes having predictable variation to changing environmental or processing parameters. As such, unimodal characteristics make
20 possible the development of ascertainable indicia for comparative evaluation of the functionally related components that make up a hydrocarbon material. Ascertainable indicia can make the response of hydrocarbon materials to such environmental or processing parameters predictable. Unimodal characteristics may also provide objective indicia for the manufacture of hydrocarbon material products to assure that components
25 have an anticipated degree of association. As can be understood, conventional technology has focused upon evaluation of the characteristics of separated components of hydrocarbon materials. The data obtained by evaluation of these isolated components is then typically used to determine the differences between types of hydrocarbon materials. However, conventional evaluation of isolated components does not provide a substantial
30 amount of information about the intact hydrocarbon material itself. It can be understood that while conventional technology may understand that a hydrocarbon materials can be made up of chemical components, or that conventional technology may understand that

the chemical components have a certain physical relationship or distribution with respect to one another, conventional technology may provide, if at all, only a limited insight about the dynamic behavior of the various components of a hydrocarbon materials to changing environmental or processing parameters, or how the components functionally
5 relate to maintain the stability of their physical association. As such, conventional technology may not provide suitable indicia of stability, thresholds of instability, or the methods for comparing such indicia of stability to such thresholds of instability which are the ascertainable measures of the unimodal characteristics of intact, unseparated hydrocarbon material. Indeed, conventional technology affords few, if any, tools for
10 diagnosing or predicting how a hydrocarbon material will behave under a specific set of circumstances.

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be formation of carbon rich material during non-pyrolytic events (at or below about 340° C). The deposition of carbon rich material, such
15 as coke, can result in fouling of heat exchange devices, or other refinery equipment in both upstream and downstream operations. This equipment may have to be shut down for mechanical coke removal as disclosed by Schabron, J. F. et al., Deposition From Heavy Oils, pp. viii and 2, (2000), hereby incorporated by reference.

Another significant problem with conventional technology for the evaluation and
20 processing of hydrocarbon material may also be the formation of carbon rich deposits, such as coke, from pyrolytic events (at or above about 340° C). Deposition of carbon rich material, such as coke, from pyrolytic events during processing can also result in the problems described above including having to shut down processing equipment for mechanical removal of the deposited materials.

25 Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be the lack of a method or use of arbitrary criteria for predicting the proximity of a hydrocarbon material to the point of transition from a homogenous mixture of components to a heterogenous mixture of components, including the proximity to carbon deposition or coke formation.

30 Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be a low yield of liquid distillates. The use of arbitrary criteria to assess the stability of a homogeneous mixture of hydrocarbon

materials, or to predict when carbon deposition may occur, can result in distillation parameters for the hydrocarbon material that stop the distillation sooner than need be to avoid deposition of carbon rich materials, such as coke. When distillation is stopped sooner than is necessary to avoid carbon deposition, it can result in less than maximal product yield from the hydrocarbon material. In 1997, for example, the average United States atmospheric and vacuum distillation refinery capacity was about 23 million barrels per day as disclosed by the Department of Energy, OIT Report, p. 5, (1998), hereby incorporated by reference. Solvent deasphalting capacity was about 0.3 million barrels per day. About 1.8 million barrels per day of heavy end feedstocks produced in 1997 from atmospheric and vacuum distillation columns and solvent-deasphalting units were input to thermal cracking and coking operations. This represents about 10% of the crude run. Id. at p. 49. An additional 6.5 million barrels per day went into catalytic cracking and hydrotreating units. Based on the total of 1.8 million barrels of total heavy ends minus about 0.3 million from solvent deasphalting, about 1.5 million barrels of heavy ends per day of thermal cracking and coking feed are produced from distillation operations. Assuming a one percent increase in United States distillate output because of efficiency improvements, an increase of about 15,000 average barrels per day of distillate and a corresponding reduction of heavy ends would result. Efficiency increases well above 1% could be possible if the proximity to carbon deposition or coking for a hydrocarbon material could be measured.

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be the inefficient use of energy. Coking operations use about 166,000-258,000 Btu per barrel of hydrocarbon material feed. Department of Energy, OIT Report, pp. 62-63, (1998). Hydrotreater energy use is comparable, and a similar consideration may apply. Since most of the energy used can be to initially heat all of the hydrocarbon feed material for distillation, there may be only minimal extra heat required to obtain a 1% improvement of distillate output at a particular temperature. For each 1% decrease in hydrocarbon material feed, there would be a potential savings of about 2.5-3.9 billion Btu with respect to hydrocarbon materials that do not need to be heated for coking, since they will have been recovered in an optimized distillate stream.

Another significant problem with conventional technology for the evaluation and

processing of hydrocarbon material may be high emissions. An energy savings of about 2.5-3.9 billion Btu per day, as discussed above, can result in a corresponding lowering of emissions from fuel that is not burned in processing operations. For example, residual fuel used as the heat source produces about 174 pounds of carbon dioxide per million Btu generated Department of Energy, OIT Report, pp. 27, (1998). Thus, in the U.S., the reduction in carbon dioxide emissions for each 1% industry-wide efficiency improvement may be about 218-679 tons per day!

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be financial losses. The disruption of hydrocarbon material processing from fouling due to deposition of carbon rich material, such as coke, is pervasive throughout the industry. The financial losses due to unscheduled downtime events as a result of non-pyrolytic, or of pyrolytic, deposition of carbon rich materials such as coke, may be difficult to quantify, but they are important.

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be that the liquid products of distillation may be of lower quality. Interrupting the distillation process, or proceeding with the distillation process in steps or stages, to avoid deposition of carbon rich materials or coke may allow for contamination of the liquid distillates.

Yet another significant problem with existing methods of processing hydrocarbon materials may be lack of a method for predicting the amount of initial deposition of carbon rich material or coke formation upon pyrolysis of a hydrocarbon material.

Still another significant problem with existing methods of processing of hydrocarbon materials may be the lack of apparatus or methods that are practical, convenient, or provide for real time data with respect to the stability of hydrocarbon materials.

With respect to processing hydrocarbon materials in general and specifically with respect to characterizing the dynamics of unseparated, intact hydrocarbon materials including predicting proximity to carbon deposition or coke formation, it can be understood there exists an array of problems which have remained unresolved by use of conventional hydrocarbon processing technology. The present invention addresses each of the above-mentioned problems and provides practical solutions.

III. DISCLOSURE OF THE INVENTION

Indicia which define unimodal characteristics of hydrocarbon materials, or indicia which estimate the stability of such unimodal characteristics of hydrocarbon materials which may be used separately or may be used in combination, or may be used in comparison to determined threshold of instability for such unimodal characteristics, to assist in determining the proximity of such unimodal characteristics to formation of multimodal characteristics, or to assist in predicting the degree of acquired multimodal characteristics in response to various processing parameters.

Naturally, as a result of these several different and potentially independent aspects of the invention, the objects of the invention are quite varied.

A broad object of a particular embodiment of the invention can be to establish values for various associations between components of a hydrocarbon material which define the attributes or characteristics of a unimodal system. One aspect of this object can be to provide a value for the size of a core material in comparison to the size of the core material having sufficient solvent solvation shell to maintain unimodal character (K_s). A second aspect of this object can be to provide an average value for the relative size ratio of a plurality of solvated core materials to the size of the plurality of solvated core materials having sufficient associated solvent (for example trapped solvent between them) to maintain unimodal character (K_F). A third aspect of this object can be to provide a value for the solvation shell and associated solvent about a core particle or plurality of core particles to maintain unimodal characteristics (K) where $K = K_s \cdot K_F$.

A second broad object of a particular embodiment of the invention can be to provide indicia of stability for the above-mentioned unimodal characteristics exhibited by hydrocarbon materials. Indicia of stability are values that result from measuring the degree of association between certain components in the hydrocarbon material which can allow assessment of the stability of a unimodal characteristic at a given point in time. Having objective values that reflect the instant degree of stability of the unimodal characteristics can be useful in evaluating suitability of hydrocarbon materials for various types of processing parameters, or for maintenance of unimodal characteristics during hydrocarbon processing.

Another broad object of a particular embodiment of the invention can be to establish thresholds of instability. A threshold of instability establishes a degree of

association (or lack of association) between components of a hydrocarbon material at which acquisition of multimodal characteristics by the hydrocarbon material may be expected. These thresholds of instability may be used in conjunction with the above-mentioned indicia of stability to assess the proximity of hydrocarbon materials having unimodal characteristics to the threshold of instability or to acquisition of multimodal characteristics.

Another object of a particular embodiment of the invention can be to provide indicia of stability or to establish thresholds of instability based upon instrumented measurement of various size ratios which correlate with unimodal characteristics. The size ratio of the core material to the core material with associated solvent (K_s), or the size ratio of a plurality of solvated core materials in comparison to the size of the plurality solvated of core materials with associated solvent (such as trapped solvent between them) (K_F), or the solvation shell about a core particle or plurality of core particles (K) where $K = K_s \cdot K_F$, independently or in combination can be useful in measuring unimodal character of a hydrocarbon material. These size relationships may be evaluated by the use of various instrumented techniques such as nuclear magnetic resonance spectroscopy, nuclear magnetic resonance tomography, mass spectrometry, infrared spectrometry, raman spectroscopy, size exclusion chromatography, gel electrophoresis device, and paper chromatography.

Another object of a particular embodiment of the invention can be to provide indicia of stability related to the molecular weight of particular components in a hydrocarbon material which correlate with the stability of unimodal characteristics.

Another object of a particular embodiment of the invention can be to provide indicia of stability based upon the distribution of various polar components in hydrocarbon materials. One aspect of this embodiment of the invention may be an indicia of stability determined as the amount of asphaltenes soluble in particular solvent having a particular polarity. For example, the amount of asphaltenes precipitated with heptane soluble in cyclohexane can be diagnostic of the stability of the unimodal character of hydrocarbon materials. A second aspect of this embodiment of the invention can be an indicia of stability determined as the ratio of the weight percent of solvent soluble asphaltenes to the weight percent asphaltenes that are not solvent soluble. For example, the ratio of the weight percent of the cyclohexane soluble portion of the

heptane precipitated asphaltenes to the weight per cent of the heptane precipitated asphaltenes appears to provide a sensitive indicator of stability of the unimodal character of hydrocarbon materials. A third aspect of this embodiment of the invention can be an indicia of stability based upon titration data. This involves the a titration of solutions of
5 hydrocarbon material with a weak solvent to the point of asphaltene precipitation. An indicia of stability can be described based on the titration data defined as p_a/C_{min} .

Another object of a particular embodiment of the invention can be to use the determined indicia of stability in comparison to the established thresholds of instability to assess the proximity of unimodal characteristics to the threshold of instability. One
10 aspect of this object of the invention can be to predict the proximity of a hydrocarbon material to coke formation.

Another object of a particular embodiment of the invention can be to use the indicia of stability, individually or in combination to evaluate hydrocarbon materials prior to processing or during processing to model substantially continuous distillation
15 parameters for a particular hydrocarbon material or mixture hydrocarbon materials.

Another object of a particular embodiment of the invention can be optimization of the yields of distillable liquids from a hydrocarbon material having unimodal characteristics. Any increase in the yield of distillable liquids from the same amount of hydrocarbon material such as heavy oil or petroleum residuum provides an immediate
20 increase in revenue. As such, a method of optimizing yields of distillable liquids has immediate and important commercial applications.

Another object of a particular embodiment of the invention can be to predict the degree of multimodal characteristics that may be acquired by a particular hydrocarbon material with respect to various processing parameters. One aspect of this object may be
25 to predict the initial amount of carbon rich material, such as coke, that may be formed upon processing of a hydrocarbon material with particular processing parameters.

Another object of a particular embodiment of the invention can be to save energy. There may be a significant energy savings involved when a higher yield of distillates is produced from the same amount of hydrocarbon material. As described above, there
30 may be only a minimal amount of extra heat required for a 1% improvement of distillate output at a particular temperature since the majority of the energy is used to initially heat all the hydrocarbon material for distillation. For each 1% decrease in the amount of

distillate bottoms heated for a subsequent coking operation in the United States a potential savings in energy of about 2.5 billion Btu to about 3.9 billion Btu per day may be realized.

Another object of a particular embodiment of the invention can be to reduce
5 emissions. The above-mentioned potential savings in energy of about 2.5 billion Btu to about 3.9 billion Btu results in a corresponding reduction in emissions from fuel that is not burned in processing additional hydrocarbon material. For example, residual fuel used to as the heat source for processing produces about 174 pounds of carbon dioxide per million Btu generated. Department of Energy, OIT Report, p. 27 (1998), hereby
10 incorporated by reference. Thus in the United States, the reduction in carbon dioxide emission for each 1% industry-wide efficiency improvement is about 218-679 tons.

Another object of a particular embodiment of the invention can be to produce higher initial quality as compared to conventional liquid distillables. Because the process of distillation may be nearly continuous, the distillates may have fewer
15 opportunities to collect water and become otherwise contaminated. This may result in higher purity distillates and perhaps lower post distillation processing costs. As such, distillates from near continuous distillation processes made possible from the instant invention may be distinguishable from conventional distillation products.

Still another object of a particular embodiment of the invention can be to provide
20 a molecular weight/polarity map system to assess the solubility of various components in a mixture of asphaltene complexes at various distillation parameters. Such a map system may provide an evaluation method for diagnosing processing conditions for hydrocarbon materials having unimodal characteristics prior to or during distillation.

Yet another object of a particular embodiment of the invention can be to establish
25 a sequential solvent extraction system to isolate various asphaltene complexes from hydrocarbon materials having unimodal characteristics based on molecular weight or polarity.

Naturally further objects of the invention may be disclosed throughout other areas of the specification and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the relationship between solubility and solubility parameter

difference.

Figure 2 shows the effects of molecular weight and solubility parameter difference on solubility.

Figure 3 shows a flow diagram of the hydrocarbon material solvent extraction sequence and solubility parameters of solvents.

Figure 4 shows a molecular weight polarity map.

Figure 5 shows elution profiles of high performance size exclusion chromatography of various amounts of material A from fraction 4 .

Figure 6 shows elution profiles of high performance size exclusion chromatography of maltenes.

Figure 7 shows titration results for three stripper bottoms.

Figure 8 shows weight percent coke relative to values for the indicia of stability_{pa/Cmin.}

Figure 9 shows weight percent coke relative to values for the indicia of stability_{y/x} based upon the weight percent of precipitated asphaltenes soluble in a second solvent over the weight percent of precipitated asphaltenes.

Figure 10 shows weight percent coke relative to values for the indicia of stability_{Ks.}

Figure 11 shows weight percent coke relative to values for the indicia of stability_{KF.}

Figure 12 shows weight percent coke relative to values for the indicia of stability_{K.}

Figure 13 shows a graph of weight percent coke relative to values for the indicia of stability_{φFS.}

V. MODE(S) FOR CARRYING OUT THE INVENTION

Hydrocarbon materials, such as heavy oils, petroleum residua, coal tars, shale oils, asphalts, or the like can comprise polar core materials, such as asphaltenes, dispersed in lower polarity solvent(s). Intermediate polarity material(s), usually referred to as resin(s), can associate with the polar core materials to maintain a homogeneous mixture of the components. The invention focuses on novel unimodal characteristics which are ascertainable aspects of the relationship, or degree of association, between these components that can maintain the hydrocarbon material as a homogeneous mixture.

Alternately, the lack of, or diminishment of these ascertainable aspects of the unimodal character can be used to predict the onset or degree of acquired (and perhaps undesirable) multimodal characteristics associated with formation of the resulting heterogeneous mixture.

- 5 As one example, refinery processes, including but not limited to, atmospheric or vacuum distillation, visbreaking, hydrocracking, delayed coking, Fluid Coking, FLEXICOKING, or Eureka that convert hydrocarbon materials to lighter distillate fuels require heating for distillation, hydrogen addition, or carbon rejection (coking). However, when using conventional refinery processes, the efficiency of converting such
- 10 hydrocarbon material may be limited by transition of the hydrocarbon material of homogeneous mixture to a hydrocarbon material of heterogeneous mixture. The transition to the heterogeneous mixture may include the formation of insoluble carbon-rich coke deposits, including the formation of coke. As such, any reduction in carbon deposition, or increase in the distillation yield during the thermal processing of hydrocarbon material
- 15 can have a significant impact on the manner or economics of hydrocarbon processing.

- The invention, in contrast to conventional processing technology, provides ascertainable unimodal characteristics as the basis for measures of stability with respect to hydrocarbon materials that transit between homogeneous mixtures and heterogeneous mixtures of components, methods for assessing the degree of the such unimodal
- 20 characteristics, methods for predicting the proximity of hydrocarbon materials having unimodal characteristics from the threshold of acquiring multimodal characteristics, or methods for predicting the degree of multimodal characteristics acquired due to various processing parameters.

- Specifically, the invention provides indicia of stability, thresholds of instability,
- 25 methods for comparing such indicia of stability with such thresholds of instability so that hydrocarbon materials can be evaluated for processing, for selecting processing parameters to avoid carbon deposition, or for reaching predetermined levels of carbon deposition, for increasing the yield of liquid distillates, for decreasing emissions from processing, or for reducing the consumption of energy. In this application, each are
- 30 disclosed as part of the results shown to be achieved by the various methods and devices described and as steps which are inherent to utilization. In addition, while a variety of methods are disclosed, it should be understood that these are accomplished using certain

devices but also that the methods and devices can varied in a number of ways.

Importantly, as to all of the foregoing, all of these facets should be understood to be encompassed by this disclosure.

The dissolution of a material in a solvent, or the mixing of two liquids to form a
5 homogeneous mixture, will occur if the free energy of the process is zero or negative as described by:

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the free energy, ΔH is the heat of mixing, T is the temperature, and ΔS is the change in entropy. Typically in a dissolution process, the entropy term is relatively
10 large, and the heat of mixing determines if the mixing will occur.

The heat of mixing may be described as:

$$\Delta H = V ((\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2})^2 \Phi_1 \Phi_2$$

where ΔH is the heat of mixing, V is total volume, ΔE_x is the molar energy of vaporization of component x , V_x is the molar volume of component x , and Φ_x is the
15 volume fraction of component x in the solution. The term $(\Delta E/V)^{1/2}$ is called the solubility parameter δ and is typically given in units of $(\text{cal/cc})^{1/2}$, called the Hildebrand. Numerical values for the solubility parameter of a solvent can be calculated as:

$$\delta = (\Delta E/V)^{1/2}$$

from the molar energy of vaporization to the ideal gas state, ΔE and the molar volume
20 V . For large molecules or polymeric systems, group contributions can be used to calculate if the density of the material is known or can be estimated.

The heat of mixing two materials is dependent on the difference between their solubility parameters squared, $(\delta_1 - \delta_2)^2$. If the solubility parameters are identical, the heat of mixing is zero and the dissolution/mixing process is driven by the entropy term
25 $T\Delta S$ alone, and mixing will occur. If the solubility parameters are not identical, the term $(\delta_1 - \delta_2)^2$ will have a net positive value, which will cause the energy term ΔH to oppose the entropy term. If the entropy term is less than the energy term, mixing or dissolution will not occur.

However, the use of the solubility parameter is complicated by the presence of dipole and hydrogen bonding interactions. For solvents or materials with strong polarity or hydrogen bonding components, dissolution may not be predictable by the single component, or dispersion solubility parameter, described above. For such systems, 5 solubility is maximized when all the components for the solvent and material being dissolved are similar in polarity. Two- or three-dimensional maps can be used to describe so-called solubility zones, areas, or spheres for such systems. Mixtures of solvents with different solubility parameter components can be used to generate a mixture with custom-formulated solubility parameter components. Thus, it is possible to 10 formulate a mixture of two or more solvents that will dissolve a material that is not soluble in one or more of the solvents alone. For hydrocarbon materials such as petroleum residua or fractions isolated therefrom, solubility characteristics can best be described by the single-component dispersion solubility parameter. Multi-component solubility parameters are not necessary.

15 Selected solvents that do not have significant polarity or hydrogen bonding components are listed in Table 1, along with their solubility parameters. The solubility parameter of a mixture of solvents is the sum of the solubility parameter of each component times the volume fraction of that component in the mixture.

Table 1. Solubility Parameters of Solvents with Predominantly Dispersive Components

	Solvent	Solubility Parameter, δ (cal/cc) ^{1/2}
5	perfluoro-n-hexane	5.9
	iso-octane	6.9
	n-pentane	7.0
	n-hexane	7.3
	n-heptane	7.4
10	cyclohexane	8.2
	toluene	8.9
	benzene	9.2
	carbon disulfide	10.0
	diiodomethane	11.8
15		

Toluene, for example, is known to be a good solvent for hydrocarbon material such as whole petroleum residua. This is probably because the solubility parameters of whole petroleum residua components lie within about ± 2 (cal/cc)^{1/2} of 8.9, or within 6.9 - 10.9 (cal/cc)^{1/2}. Once thermal treatment of petroleum residua has begun, however, toluene fails to solvate the more polar components, which are formed as carbon deposition or coking ensues.

Relatively large solubility parameters require the use of polar interactive or hydrogen bonding solvents such as the alcohols (methanol $\delta = 14.6$, ethanol $\delta = 12.5$, etc.). Solubility parameters below those of the perfluorinated hydrocarbons can be attained by using silicone oils or supercritical fluids such as supercritical carbon dioxide.

Hydrocarbon materials, such as petroleum residua, are usually complex mixtures that are usually separated into well-defined fractions prior to characterization. Separation schemes typically include steps such as precipitation of asphaltenes by a hydrocarbon solvent such as n-heptane and subsequent separation of the deasphalted material (maltenes) by adsorption, ion exchange, size exclusion chromatography, or combinations

thereof as disclosed by Schabron, J.F., G.W. Gardner, J.K. Hart, N.D. Niss, G. Miyake, and D.A. Netzel, The Characterization of Petroleum Residua, United States Department of Energy Report DE/MC/11076-3539 (1993), hereby incorporated by reference. The isolation of components from hydrocarbon materials, such as asphaltenes, can be based
5 upon a solvent separation procedure based on the solubility difference between the precipitating solvent and the precipitated material. The solubility (or lack thereof) of components of hydrocarbon materials can be dependent on both molecular weight and polarity considerations. The solubility parameter of a particular hydrocarbon material or residuum fraction probably constitutes a range that is reflective of the variety of chemical
10 components of the fraction. The solubility parameter difference that results in a phase separation of two materials, such as asphaltenes in a solvent can be estimated using the Scatchard-Hildebrand equation, which involves several assumptions that take into account both the heat of mixing and entropy terms:

$$\ln a_a = \ln x_a + M_a/RT\rho_a \cdot [N_s^2(\delta_s - \delta_a)^2]$$

15 where a_a is the activity of the solute a , x_a is the mole fraction solubility of a , M_a is the molecular weight of a , ρ_a is the density of a , N_s is the volume fraction of solvent, and $(\delta_s - \delta_a)$ is the difference between the solubility parameters of the solute a and the solvent s . Assuming that the activity of asphaltenes a_a is 1 (solid asphaltenes in equilibrium with dissolved asphaltenes as an example) and the volume fraction of an excess of solvent is
20 essentially 1, the equation can be rearranged into a form that can be used to gain insight into the solubility of asphaltenes:

$$\ln x_a = -M_a/RT\rho_a \cdot [(\delta_s - \delta_a)^2]$$

Assuming molecular weights of 750 and 1,500 g/mole for two hypothetical
25 asphaltene molecules, the solubility as a function of the differences between solubility parameters of the asphaltene molecules and a range of solvent solubility parameters can be calculated.

Referring now to Figure 1, it can be understood that the solubility of an individual asphaltene molecule or complex decreases as the difference between solubility

parameters increases. Also, a lower molecular weight molecule is more soluble than the higher molecular weight molecule for a particular difference in solubility parameter.

From the above equations, it is apparent that the solubility depends both on molecular weight and polarity of the particular asphaltene molecule or associated specie. In an

5 asphaltene mixture, for example, there exists a polarity and molecular weight continuum as described by Schabron, J.F. and J.G. Speight, *The Solubility and Three-Dimensional Structure of Asphaltenes*, Petroleum Science and Technology, 16 (3-4), pp. 361-376 (1998), hereby incorporated by reference.

Now referring to Figure 2, additional information can be gleaned by calculating
10 the solubility parameter difference at several molecular weights ranging from 100 - 10,000 g/mole at which the solubility of asphaltenic or other material is a mole fraction of about 0.001 (0.1 %, or 1,000 ppm). The results of this calculation defines a phase diagram that is a function of molecular weight and solubility parameter difference. As can be understood from the figure both polarity and molecular weight of asphaltenes in a
15 solvent define the solubility boundary. This conceptually describes how asphaltenes can be precipitated from hydrocarbon materials, which can be considered a type of homogeneous mixture having a continuum of molecular weights and polarities which exhibit or have certain unimodal characteristics. Figure 2 also shows in a generalized manner that as the molecular weight of a particular solute decreases, there is an increased
20 tolerance to polarity difference between solute and solvent under miscible conditions.

The absolute difference in solubility parameters that will result in transition from the homogeneous mixture exhibiting unimodal characteristics to the heterogeneous mixture exhibiting or having multimodal characteristics such as a two-phase system (or other poly-phase system), or precipitation of a component, or deposition of carbon, for a
25 particular system is not straightforward. Based on the above discussions and the results illustrated in Figure 2, some generalizations can be made. For a polymer to dissolve in a solvent, the solubility parameter of the solvent should be within about $1 \text{ (cal/cc)}^{1/2}$ of the solubility parameter of the polymer. For a non-polymeric solid material, such as naphthalene, to dissolve in a solvent, the difference in solubility parameters should be
30 less than about $2 \text{ (cal/cc)}^{1/2}$. And finally, for two liquids to be miscible, the difference in their solubility parameters should be less than about $1 \text{ (cal/cc)}^{1/2}$.

Now referring to Figures 3 and 4, and the above discussion, an embodiment of

the invention can be a molecular weight - polarity map developed specifically for hydrocarbon material components. A molecular weight - polarity map can have a first axis having values relating to molecular weight. It may also have a second axis having values relating to solubility parameter. As can be understood, a particular molecule or associated specie in a hydrocarbon material occupies a single point, or molecular weight - polarity coordinate location (3) on, on the map. A mixture of molecules or mixture of molecules with associated species forming a continuum of polarity or apparent molecular weight values or a combination of both (either of individual molecules or individual molecules with associated species) can be visualized as occupying a particular area on the map. For a particular solvent, the solubility of a solute increases with decreasing polarity, decreasing apparent molecular weight, or a combination of the two. As a hydrocarbon material undergoes thermal alteration, solvent perturbation, or aging, the changes in the molecules or associated species can cause the points representing these materials to move to a different region of the map. This movement can illustrate at least one unimodal characteristic of hydrocarbon materials. Interestingly, the core material can comprise a variably adjustable core material having a molecular weight responsive to temperature change. Also, it is important to note that the core material may have polarity which is stabilized within a region of solubility even when the molecular weight may change. Thus, such a map can be used as a means of evaluating the characteristics of hydrocarbon materials or diagnosing processing conditions or the state of thermal degradation. It can also be used as a tool in efforts to diagnose and possibly intervene in the incipient precipitation of polar materials during hydrocarbon material processing.

One embodiment of the phase diagram map can be developed by calculating the core material solubility regions, including the solubility region of asphaltenes, by determining solubility of core materials or asphaltenes in a variety of solvents. For example, solvents ranging from iso-octane, with a solubility parameter of $6.9 \text{ (cal/cc)}^{1/2}$, to carbon disulfide, with a solubility parameter of about $10.0 \text{ (cal/cc)}^{1/2}$. As shown by Figure 4, the core material solubility region (1) can comprise between about $6.9 \text{ (cal/cc)}^{1/2}$ to about $11.0 \text{ (cal/cc)}^{1/2}$. The map can be based on solubility-parameter-tuned solvent mixtures providing even spacing between a plurality of solvent tuned contour lines (Δ) of about $0.2 \text{ (cal/cc)}^{1/2}$, except for the last series between toluene: CS_2 (55:45)(v/v) and CS_2 , where the spacing can be $0.6 \text{ (cal/cc)}^{1/2}$. The border between the

soluble and insoluble regions is defined arbitrarily as the solubility of a mole fraction of 0.001 (0.1 %, or 1,000 ppm). This border is actually a point on a solubility gradient, where solubility increases towards the left-hand portion of a curve and decreases to the right. Naturally, other solvents or combinations of solvents could be used to create a

5 range of solubility parameters having a different number or spacing with respect to the solvent tuned contour lines. As shown by Figure 4, a particular embodiment of the molecular weight -polarity map can be established by using a first solvent tuned contour line based on iso-octane, a second solvent contour line based on heptane, a third solvent tuned contour line based on heptane:toluene (2:1)(v:v), a fourth solvent tuned contour

10 line based on heptane:toluene (1:2)(v:v), a fifth solvent tuned contour line based on toluene, a sixth solvent tuned contour line based on toluene:carbon disulfide (55:45) (v:v), and an eighth solvent tuned contour line based on carbon disulfide.

The molecular weight - polarity related coordinate location (3)(for clarity not all the coordinate locations have leaders and identification numbers) of a particular material

15 on the map was determined by three measurements. First, a solubility or solvent spectrum of the material was obtained to determine between what lines on the map the material lies. This was accomplished by performing a series of solubility measurements in a series of solvents of increasing or decreasing solubility parameters and determining their weight percentages of the soluble material. Excess solvent to solute (40:1 v:w)

20 ratios were used to minimize any potential effect of the solute on the overall solubility parameter of the system. Second, a number average molecular weight of the molecules or associated species mixture was determined on the isolated fractions using vapor pressure osmometry in toluene at 60° C. Third, the isolated fractions were analyzed using analytical-scale size exclusion chromatography.

25 Ideal materials for demonstrating how the molecular weight- polarity map invention may apply to thermally treated hydrocarbon material having unimodal characteristics are bench-scale stripper bottoms oils (although the example is not meant to reduce the scope of invention to such materials or to such scale) which were generated as listed below:

- 30
- A. Stripper Bottoms - 273 °C (525 °F)
 - B. Stripper Bottoms - 345 °C (650 °F)
 - C. Stripper Bottoms - 371 °C (700 °F)

These three stripper bottom represent a series of increasing severity of thermal treatment at atmospheric pressure for the same hydrocarbon material. In the sequence of increasingly severe treatment, the A bottoms were fed into the B unit, whose bottoms were fed into the C unit. These particular materials were allowed to remain in the 5 strippers as they cooled down. Both Materials A and B were fully soluble in toluene, while Material C contained 13.5 weight percent toluene insoluble material, which yielded 17.9 weight percent ash.

With respect to the first measurement, as discussed above and now referring to Figure 3, a solubility or solvent spectrum of the material was obtained using the solvent 10 extraction sequence illustrated. All solvents used were reagent grade or better from commercially available sources. Iso-octane asphaltenes were first obtained by heating the whole residua with a 40:1 (v:w) portion of iso-octane to about 70 °C for 1 hour with stirring. The mixture was stirred at room temperature overnight, then allowed to set for at least 0.5 hour prior to vacuum filtering through a medium frit (10-15 µm) sintered 15 glass filter. To remove solvent from the insolubles, air was passed through the filter for 5 min, they were placed in a vacuum oven at 120 °C and 23 inches Hg vacuum for 1 hour, were cooled, then weighed. A 40:1 ratio (v:w) of n-heptane was mixed with the insolubles and stirred overnight. The insolubles were filtered using vacuum filtration through a medium glass filter. These steps were repeated with the series of solvents 20 shown in Figure 4. At the end of the series, the carbon disulfide insolubles (including coke) were ashed in a muffle furnace at 400 °C overnight to obtain weight percent ash.

With respect to the second measurement, number average molecular weights were determined with a Knauer vapor pressure osmometry (VPO) instrument using toluene at 60°C (ASTM D-2503). Determinations were made with 1- 4 weight percent 25 sample solutions. Benzil was used for calibration.

With respect to the third measurement, high-performance analytical scale size exclusion chromatography (SEC) results for the fractions are listed in Table 3. Portions of 150 µL of 0.2 weight percent solutions of the fractions were injected (0.3 mg). The values are reported relative to polystyrene standards having known molecular weight 30 analyzed under the same conditions. As such, the standards must be used with caution since polystyrene and the hydrocarbon material or residua components are different materials.

The compiled data for the three stripper bottoms materials are presented in Table 2. Again referring to Figure 4, the molecular weight - polarity map invention developed from the data and the effects of the thermal treatment on the three heavy oils prior to and during coke formation. The molecular weight - polarity map invention "peels" the layers of association with respect to a hydrocarbon material having unimodal characteristics. The gravimetric data show the progression towards more polar species as the severity of thermal treatment increases. Material C is generating both carbon or coke, or carbon or coke precursors (Fractions 6 and 7).

Table 2. Solubility Map Data for Three Stripper Bottoms

10

Sample Measurement		Fraction (See Figure 3.)								coke	ash
		1	2	3	4	5	6	7			
15	A	Weight Percent	85.9	0.8	6.3	5.1	0.7	1.1	0.1	<0.1	<0.1
		VPO Mn g/mole	474	1260	4040	17000	23000	—	—	—	—
		δ (cal/cc) ^{1/2}	8.4	9.2	8.8	8.8	9.2	—	—	—	—
	B	Weight Percent	83.4	0.9	6.7	5.5	1.0	2.2	0.1	0.2	<0.1
		VPO Mn g/mole	542	1180	3580	12000	14000	—	—	—	—
		δ (cal/cc) ^{1/2}	8.4	9.2	8.8	8.8	9.2	—	—	—	—
20	C	Weight Percent	64.0	2.0	5.3	5.8	2.9	4.5	1.5	11.5	2.5
		VPO Mn g/mole	516	684	1320	2920	6800	—	—	—	—
		δ (cal/cc) ^{1/2}	9.0	9.9	9.6	9.5	9.5	—	—	—	—

The data also show that the number average molecular weights of the iso-octane-soluble maltenes are about the same for all three oils. The molecular weight of each of the more polar fractions decreases significantly with thermal treatment. The main difference between the various polar fractions for a particular material seems to be molecular weight. The solubility parameters are similar for a particular series of polar materials with large differences in apparent molecular weight. This leads to the speculation that a residua colloidal system self-adjusts to lower the overall energy of the system by matching as closely as possible the polarity of the associated complexes to the solvent matrix (iso-octane maltenes). This appears to occur by automatic adjustment of the apparent molecular weights of the complexes.

For the pyrolysis series, the higher molecular weights are probably due to associated species, which the thermal treatment is breaking apart. This results in an overall less stable colloidal-type system with increasing severity of thermal treatment, as was observed with the Heithaus titration data discussed below. Also, significant cracking has taken place in Material C, which further reduces the apparent molecular weight of the corresponding fractions soluble in the various solvents compared to Materials A and B. The solubility parameters (polarities) of the fractions from C are larger than the corresponding fractions from A and B. The data clearly show some significant differences between Material C, and the less severely treated Materials A and B.

10

Table 2. High-Performance Size Exclusion Chromatography Results

	Fraction	Size Exclusion Chromatography			VPO	
		Mw	Mn	Range ^a	Mw/Mn	Mn
15	<u>A (273 °C/525 °F)</u>					
	1	928	422	210-2200	2.20	474
	2	1490	585	270-3400	2.55	1260
	3	2440	772	340-5600	3.16	4040
	4	2240	618	260-5400	3.62	17000
20	5	2120	523	210-5300	4.05	23000
	<u>B (343 °C/650 °F)</u>					
	1	923	439	220-2100	2.10	542
	2	1320	539	250-3000	2.45	1180
	3	2110	703	310-5000	3.00	3580
25	4	2090	611	260-5000	3.42	12000
	5	1930	510	210-4800	3.78	14000
	<u>C (371 °C/700 °F)</u>					
	1	705	395	210-1500	1.78	516
	2	788	388	190-1800	2.03	684
30	3	1140	481	220-2600	2.37	1320
	4	850	410	250-3200	2.04	2920
	5	1230	455	200-2900	2.70	6800

a. From elution volumes at 10% to 90% of peak area

Except for the number average molecular weight values for the extracted iso-octane maltenes for all three materials (Fraction 1), the values are significantly lower than the number average molecular weight values determined by VPO. The discrepancy cannot be wholly attributed to the use of polystyrene standards and the non-uniform response with refractive index detection from residual components of differing functionality. Some adsorption of materials on the polystyrene-divinylbenzene stationary phase may be occurring also. The values determined by VPO represent the apparent number average molecular weights in 1 - 4 weight percent toluene solutions. An additional possible effect may be that associative complexes that give apparent high VPO molecular weight values in solution break down during the SEC separation for Fractions 4-5 for all three materials, resulting in significantly lower apparent number average molecular weight values than the corresponding VPO values. To check this further, various amounts of one of the fractions for which sufficient material was available were injected onto the high-performance SEC column. The fraction was Material A, Fraction 4 which gave an apparent VPO molecular weight of 17,000 g/mole and a SEC number average molecular weight of 618 g/mole (Table 2).

Now referring to Figure 5, which shows the results from injections of 100 μ L of toluene solutions containing 0.3 - 15 mg onto the SEC column. As more material was injected, the retention volume decreased, indicating an increase in associations or apparent molecular weight. For the 7.5 mg injected, the peak split into two peaks, suggesting the presence of significant associations. This peak splitting and elution volume shortening phenomenon was not observed when a polystyrene standard with a molecular weight of 400 g/mole was injected under identical conditions. Thus, the peak splitting phenomenon is not likely due to overloading the column with sample. For injections of 0.3 to 7.5 mg, the material eluted in about 3 mL of toluene. The concentration at which significant complex formation begins for this asphaltenic material is estimated to be at the point where the peak splits. This occurs somewhere between 1.5 and 7.5 mg injected diluted into about 3 mL toluene elution solvent, which is between about 0.06 - 0.5 weight percent. This result may be consistent with the results of

Andersen and Birdie, who reported a critical micelle concentration of asphaltenes in toluene near 0.38 weight percent using calorimetric titration. Andersen, S.I. and K.S. Birdi, Aggregation of Asphaltenes as Determined by Calorimetry, Journal of Colloid and Interface Science, 142, pp. 497-502 (1991).

5 As can be understood from the table, as with the VPO data, the SEC number average molecular weights for a particular fraction generally decrease with increasing severity of thermal treatment. The polydispersity M_w/M_n , an indicator of molecular weight distribution, also decreases for a particular fraction with increasing severity of thermal treatment.

10 Now referring to Figure 6, chromatograms appeared as essentially symmetrical peaks with one exception — the iso-octane maltenes (Fraction 1). These chromatograms show a leading high molecular weight shoulder component (4) in the 273 °C (525 °F) material, which was smaller for the 343 °C (650 °F) material and was not evident for the 371 °C (700 °F) material. As such, this component of the iso-octane maltenes having an
15 apparent high molecular weight appears to be related to at least one unimodal characteristic of hydrocarbon materials which can be destroyed with increasing severity of thermal treatment.

An embodiment of the invention based on this finding comprises an indicia of stability_{usc} based upon the steps of detecting this unimodal characteristic stability
20 component having apparent high molecular weight. This approach may comprise providing a hydrocarbon material component analysis device, or devices in combination, which can be a size exclusion chromatography device as described above, or could also be other devices for identifying the apparent high molecular weight unimodal stability component such as a mass spectrometry device, an infrared spectrometry device, a raman
25 spectroscopy device, gel phoresis device, paper chromatography device, or nuclear magnetic resonance device. Naturally, each hydrocarbon analysis device could be configured, as would be well known to those of skill in the art, so that the unimodal characteristic stability component could be identified. While in the example above, maltenes were extracted into iso-octane, other solvents, or other devices could be used to
30 isolate the corresponding maltenes containing the unimodal characteristic stability component from the hydrocarbon material. Thereafter, detection of the unimodal stability component could comprise observing elution of the apparent molecular weight

of the unimodal characteristic stability component directly as described above for size exclusion chromatography where the apparent molecular weight can be equal to or larger than about 500 gram per mole. As the amount of the unimodal characteristic stability component approaches zero continued thermal processing results in carbon deposition including coke formation.

Now referring to Figure 7, in addition to the above-mentioned three measurements, automated Heithaus titration was performed with the toluene-soluble components of hydrocarbon material (although other dissolvents could be used such as benzene, xylene, ethylbenzene, similar aromatic hydrocarbons). This method comprises preparing three toluene solutions at different concentrations of hydrocarbon material. Each can be titrated with a weak solvent such as iso-octane (although other weak solvents could be used such as pentane, hexane, heptane, hexadecane, or similar aliphatic hydrocarbons) with a titration device. The weight of residua or asphalt (W_a), the volume of toluene (V_s), and volume of iso-octane titrant (V_t) are recorded at the flocculation point where asphaltenes just begin to precipitate for each solution. The flocculation ratio and dilution concentration are calculated as follows:

$$FR = \text{Flocculation Ratio} = V_s / (V_s + V_t)$$

$$C = \text{Dilution Concentration} = W_a / (V_s + V_t)$$

A plot of FR versus C can be made and the intercepts determined (FR_{\max} and C_{\min}). The Heithaus parameters are defined as follows:

$p_a = 1 - FR_{\max}$	Peptizability of Asphaltenes
$p_o = FR_{\max} \times (1/C_{\min} + 1)$	Solvent Power of Maltenes
$P = p_o / (1 - p_a) = 1/C_{\min} + 1$	Overall Compatibility of Residua

Larger values of p_a may indicate more peptizable asphaltenes, and larger values of P indicate an overall compatible system. A larger p_o value is subject to a mixed interpretation.

The Heithaus parameters for these three stripper bottoms materials are provided in Table 4. The results show that the three bottoms materials are becoming less stable with

increasing severity of thermal treatment. The results also show a significant difference between Material C, which is producing coke or carbonaceous material, and Materials A and B, which are not yet near coke production or carbon deposition.

Table 4. Heithaus Titration Results for Three Stripper Bottoms

Heithaus Parameter	Material		
	A (525 °F)	B (650 °F)	C (700 °F)
P_a	0.668	0.638	0.364
P_o	0.766	0.805	1.09
P	2.31	2.23	1.71
P_a/C_{min} Ratio	0.87	0.78	0.26

Another way of evaluating FR_{max} can be that it is the volume fraction of toluene in a toluene- iso-octane mixture, assuming additive volumes. By knowing the solubility parameter of both solvents, the solubility parameter at FR_{max} can be calculated. FR_{max} is thus a measure of the solubility parameter at infinite dilution at which asphaltenes begin to precipitate. Such measurements also may have applicability in predicting precipitation of asphaltenes for mixtures of two or more residua. A relatively larger FR_{max} indicates a less soluble asphaltene. Since solubility depends on both molecular weight and polarity, this can be due to a higher molecular weight or more polar asphaltene, or both. C_{min} is the ratio of residua to titrant (iso-octane for this example although other solvents can be used) at which asphaltenes begin to precipitate. A larger C_{min} indicates a less compatible system (smaller P). Assuming that asphaltene flocculation occurs at a particular solubility parameter for a particular residua, it is apparent that both FR_{max} and C_{min} and the line connecting them are at the same solubility parameter.

The solubility parameter at which asphaltenes begin to precipitate (at FR_{max}) and the solubility parameters of the residua matrix (at C_{min}) were calculated and are listed in Table 5 for the three stripper bottoms. Both the solubility parameter for the whole residua and the solubility parameter of the onset of asphaltene flocculation increase with

increasing severity of thermal treatment. The material that has been heated to the point of coke production is significantly more polar than the same material prior to coke production. This is also reflective of cracking and the removal of less polar distillates with heating.

5 Table 5. Solubility Parameters for Whole Residua and Asphaltene Precipitation Onset

Solubility Parameter, δ (cal/cc) ^{1/2}			
Material	Whole Residua	Asphaltene Precipitation Onset	
10	A (525 °F)	8.4	7.6
	B (650 °F)	8.5	7.6
	C (700 °F)	9.1	8.2

Now referring to Table 4, another embodiment of the invention based on the titration data provides an indicia of stability defined as p_a/C_{min} . This indicia of stability _{p_a/C_{min}} can
 15 be based on the above described consideration that p_a decreases and C_{min} increases as the overall stability of the unimodal characteristics decreases. A threshold of instability _{p_a/C_{min}} value for can be assigned at a value within the range of about 0.1 to about 0.4. The indicia of stability _{p_a/C_{min}} for a particular hydrocarbon material can be compared to the threshold of instability _{p_a/C_{min}} . As can be understood for residuum C in Table 4 the
 20 p_a/C_{min} has decreased from a value of 0.87 to a value of 0.26. The first value indicative of a relatively stable hydrocarbon material having unimodal characteristics while the second value suggests that the material has acquired some degree of multimodal character, which may include the formation of coke.

Now referring to Table 6, another embodiment of the invention can be an indicia of
 25 stability based upon determining the amount of precipitated asphaltenes which are soluble in a solvent having a polarity between that of the precipitating solvent and a solvent which can dissolve the precipitated asphaltenes completely. For the three stripper bottoms, as an example, asphaltenes were precipitated using heptane, although other precipitating solvents can be used including iso-octane, pentane, or hexane for
 30 example. The precipitated asphaltenes can then extracted with a second solvent, in this

example cyclohexane, having polarity that is between the precipitating solvent and a polarity which would substantially dissolve the precipitate completely. Other solvents could be used as the second solvent depending on which solvent was used as the precipitating solvent such as pentane, heptane, or heptane: toluene 1:1 (v:v).

5 Table 6. Solubility of Heptane Asphaltenes in Two Solvents with $\delta = 8.2 \text{ (cal/cc)}^{1/2}$

Material	wt.% Heptane Asphaltenes	wt.% Asphaltenes Soluble in:	
		Cyclohexane	Heptane: toluene (1:1)(v:v)
A (525 °F)	11.9	14.0	63.2
10 B (650 °F)	14.2	10.8	52.4
C (700 °F)	22.4	1.8	26.9

As can be understood from Table 6, both hydrocarbon materials A and B are fully soluble in cyclohexane, yet the heptane asphaltenes are only partially soluble. Again,
 15 this is due to the associated unimodal nature of these materials. The cyclohexane-soluble components of the asphaltenes can reflect the state of the solubilizing resins in these materials. The disappearance of the cyclohexane-soluble portion of heptane asphaltenes as the stripper bottoms are increasingly heated is illustrated by the data for the stripper bottoms and appears to coincide with acquired multimodal characteristics, including coke
 20 formation. As such, an indicia of stability reflects an observed amount of precipitated asphaltenes soluble in the second solvent.

It is interesting to note that the solvent mixture heptane: toluene (1:1)(v:v), which has the same solubility parameter as cyclohexane, $(8.2 \text{ (cal/cc)}^{1/2})$, gives a larger yield of soluble material than cyclohexane from the heptane asphaltenes for each of the three
 25 stripper bottoms. A likely explanation is that in addition to the solubility parameter, there is a chromatographic effect due to the presence of toluene in the mixed solvent. Possibly toluene is displacing some associated material from the associated asphaltene complex. Although solubility parameters of mixtures are additive with the volume fractions of the components, chromatographic solvent strengths are not. The first small
 30 portion of a stronger chromatographic solvent in a mixture with a weaker one increases

the overall chromatographic solvent strength almost exponentially. This is a plausible explanation of the data in Table 6. This also provides additional evidence for the presence of associated species in a hydrocarbon material having unimodal characteristics.

Again referring to Table 6, another embodiment of the invention can comprise an
5 indicia of stability_{y/x} be established by determining the weight percent asphaltenes soluble in the second solvent (Y) to the weight of the asphaltenes precipitated by the first solvent (X). A larger weight percent asphaltene would indicate a greater coking tendency, as would a smaller weight percent soluble portion of the asphaltenes. A threshold of instability_{y/x} can be assigned a value of between about 0.0 to about 1.0. The
10 indicia of stability_{y/x} can be compared to the threshold of instability_{y/x} to determine the proximity of a hydrocarbon material to acquiring multimodal characteristics.

The ratio values for the three stripper bottoms are 1.2, 0.76, and 0.08 for the materials treated at 273, 343, and 371 °C (525, 650, and 700 °F), respectively. The proximity of the hydrocarbon to acquiring multimodal characteristics, including coke formation, is
15 closer as the value for this indicia of stability approaches zero.

To further define aspects of the unimodal character of hydrocarbon materials, and illustrate the universal applicability of the above-described indica of stability, thresholds of instability, or their application to assessing proximity of the unimodal characteristics to acquisition of multimodal characteristics, including carbon deposition or coke
20 formation, five additional hydrocarbon materials were evaluated. These petroleum residua were Boscan, California Coastal, MaxCL, Redwater, B.C., and Vistar. While these particular residua were the focus of the following examples, their choice is not intended to limit the application of the described embodiments of the invention solely to such hydrocarbon materials. Embodiments of the invention may have application over a
25 broad range of hydrocarbon materials such as other petroleum residua, heavy oils, coal tars, shale oils, asphalts, or the like.

Now referring to Figures 8 and 9, and Tables 7 and 8, indicia of stability_{pa/Cmin}, and indicia of stability_{y/x} from the cyclohexane soluble portions of precipitated asphaltenes for the five hydrocarbon materials are illustrated. For these determinations, hydrocarbon
30 materials were pyrolyzed at 400 °C for 60 and 90 minutes. Pyrolysis experiments were conducted in a stirred batch reactor system constructed from 4-inch diameter stainless steel pipe charged with about 120 g of hydrocarbon material. The reactor was heated to

the desired set point temperature (400 °C) and held at that temperature for the duration of the experiment. At the end of the experiment, the reactor was allowed to cool and the contents of the reactor were recovered. The carbon solids or coke can be separated from the product oil by solubility in toluene.

- 5 The amount of carbon solids formed at both 60 and 90 minute residence times was evaluated in terms of the above mentioned indica of stability. Heithaus titrations could not be performed on the 90 minute pyrolysis products because of sample instability and the immediate formation of precipitate in the titration cells. Therefore, the p_a/C_{min} embodiment of indica of instability was not determined for the 90 minute products.

Table 7. Heithaus Titration Results and p_a/C_{min} Indicia of Stability

	Material	p_a	p_o	P	C_{min}	$-p_a/C_{min}$
	Redwater, B.C.					
5	Original	0.698	0.749	2.48	0.676	1.0
	Pyrolyzed 60 min.	0.422	0.753	1.30	3.19	0.13
	Pyrolyzed 90 min.	0.162	0.878	1.05	21.1	0.0076
	CA Coastal					
10	Original	0.614	1.12	2.89	0.529	1.2
	Boscan					
	Original	0.691	0.992	3.21	0.452	1.5
	Pyrolyzed 60 min.	0.245	0.905	1.20	5.00	0.049
15	Pyrolyzed 90 min.	0.285	0.717	1.00	434	0.00
	MaxCL					
	Original	0.682	0.758	2.38	0.725	0.94
	Pyrolyzed 90 min.	0.152	0.973	1.15	6.80	0.022
	Vistar					
20	Original	0.616	0.916	2.38	0.722	0.85
	Pyrolyzed 60 min	0.373	0.831	1.32	3.08	0.12

As can be understood from Figure 8, as indicia of stability p_a/C_{min} approaches about 0.1 the unimodal character of the hydrocarbon material becomes unstable which may be accompanied by carbon deposition or coke formation.

Table 8. Heptane Asphaltenes and Asphaltenes Soluble in Cyclohexane

		Weight Percent			Wt.% Toluene Insolubles (Coke)
		X: Heptane Asphaltenes ^a	Y: Asphaltenes Soluble in Cyclohexane	Y/X	
5	Residuum				
	Redwater, B.C.				
	Original	11.7	41.4	3.5	<0.01
10	Pyrolyzed				
	60 min.	15.9	14.7	0.92	0.2
	90 min.	17.1	6.0	0.35	2.9
	CA Coastal				
	Original	19.7	23.1	1.2	<0.01
15	Pyrolyzed				
	60 min.	13.9	4.5	0.32	4.4
	90 min.	11.6	5.7	0.49	7.9
	Boscan				
	Original	19.8	40.6	2.1	<0.01
20	Pyrolyzed				
	60 min.	15.6	5.3	0.34	7.5
	90 min.	12.5	2.6	0.21	11.2
	MaxCL				
	Original	18.1	45.8	2.5	<0.01
25	Pyrolyzed				
	90 min	19.8	3.6	0.18	7.0
	MaxCL				
	Original	18.0	36.8	2.0	<0.01

Pyrolyzed

60 min.	18.2	13.2	0.73	0.2
90 min.	9.5	3.8	0.40	6.2

5 a. Weight percent of toluene soluble material

Similarly it can be understood from Figure 9, that indicia of stability_{y/x} (weight percent of precipitated asphaltenes soluble in cyclohexane to asphaltenes soluble in heptane) (although other solvent pairs can be used as discussed above) approaches about 1.0 the hydrocarbon material becomes unstable which may be accompanied by carbon deposition or coke formation.

The plots dramatically illustrate the diagnostic potential of the indicia of stability and indicia of instability in measuring how close a hydrocarbon material may be to acquiring multimodal characteristics including carbon deposition such as coke formation.

Additional relationships, in addition to those described above, have also been considered in evaluating these hydrocarbon materials. As a result additional embodiments of the invention for evaluation of unimodal character of hydrocarbon materials have been delineated. As discussed above and in greater detail below hydrocarbon materials having unimodal characteristics can be considered to be a series of components functionally related by a continuum of polarity in which core materials such as polar asphaltene materials are dispersed in a solvent phase.

Extensive experimentation was conducted to create a theoretical model to analyze unimodal characteristics related to hydrocarbon material and their transition to multimodal characteristics. The experimentation was also directed to elucidate aspects of the theoretical model for unimodal character which could be practically measured or valued. The model focuses upon association of components in hydrocarbon materials. Resins and solvent layers associated about a core material of hydrocarbon materials such as asphaltene (although the core material may be other polar components of hydrocarbon materials or may include other components associated with the asphaltene), and solvated core materials interacting with each other in an ordered hydrocarbon material system.

Additional solvent can be associated with or trapped between the solvated core material

The model defines a hydrocarbon solvation shell magnitude term K ($K=K_s \cdot K_f$)

representing the amount of solvent adsorbed around a core material such as an asphaltene (K_S) or the solvent associated with or trapped by a group of solvated core materials (K_F) in an ordered unimodal system. For hydrocarbon materials such as the petroleum residua evaluated, K values ranging from 3-6 at 25°C can be typical. As a hydrocarbon material is heated K decreases, indicating a decreasing amount of trapped solvent associated with the solvated core materials in the hydrocarbon material and flocculation of the core material may result. This may be a reversible process on cooling, unless pyrolysis reactions begin, at temperatures above 340 °C. Solvation constants (K) are derived using:

10

$$K_S K_F \equiv K = \frac{1 - \eta_{rel}^{-0.4}}{\chi_a / 1.2}$$

In the equation, K is the overall solvation constant for the hydrocarbon material, K_S is the ratio of the size of the solvated core material to the size of the core material itself, K_F is the amount of solvent otherwise associated with the solvated core materials, χ_a is the mass fraction of heptane asphaltenes, divided by an assumed density of 1.2 grams per cubic centimeter to yield the size fraction of the core materials, and η_{rel} is the relative viscosity. To estimate relative viscosities, core material precipitation with can be performed with a solvent such as heptane. Zero shear viscosities (η , cps) are measured for a hydrocarbon material and for the corresponding heptane maltenes (η° , cps). The ratio of η/η° is called the relative viscosity (η_{rel}) and is diagnostic of the manner in which core materials such as asphaltenes are suspended in a solution of maltenes. This value is somewhat dependent on the solvent used to precipitate the asphaltenes and is related to the state of peptization. A higher relative viscosity indicates a more significant unimodal characteristic. The effective core material volume fraction, ϕ_{eff} is given by multiplying K by the volume fraction of heptane asphaltenes.

$$\phi_{eff} = K \chi_a / 1.2$$

values of K for a hydrocarbon material can indicate whether or not unimodal character is present. The value of K_S can depend on the experimental data used. For

example, relative viscosities using heptane or iso-octane maltenes may vary somewhat. Results from the determination of K_S using more than one approach, for a wide selection of hydrocarbon materials having unimodal characteristics, show that for unpyrolyzed hydrocarbon material such as petroleum residua the typical value of K_S is 1.6. With
5 pyrolysis (>340 °C), there is a carbon deposition or coke induction period during which a multimodal system begins to form as discussed by Schabron, J.F., A.T. Pauli, and J.F. Rovani, Jr., Petroleum Residua Solubility Parameter/Polarity Map: Stability Studies of Residua Pyrolysis, WRI Report 99-R004 to DOE under Cooperative Agreement DE-FC26-98FT40322 (1999), hereby incorporated by reference. With continued pyrolysis,
10 carbon deposition or coke begins to form as the unimodal characteristics have broken down irreversibly. When this occurs, relative viscosity measurements have no validity. Thus, to estimate K_F and K_S for pyrolyzed hydrocarbon materials, alternative calculations can be used. In these equations, χ_{cy}

$$K_S = \frac{1}{1 - \chi_{cy}} \qquad K_F = \frac{1}{1 - p_a}$$

is the weight fraction of heptane asphaltenes soluble in cyclohexane, and p_a is the
15 Heithaus parameter, each as described above.

Now referring to Figures 10, 11, and 12, and Table 9, the theoretical basis for additional embodiments of the invention becomes evident when values for these terms are determined before and after pyrolysis at various severities. Table 9 lists the values of K_S , K_F , and K and weight percent carbon deposition or coke for the five residua. The
20 data are plotted in Figures 10, 11, 12, respectively.

Table 9. K_S , K_F , and K values for the Original and Pyrolyzed Residua

Residuum		$K_S = (1/(1-\chi_{cy}))$	$K_F = (1/(1-p_a))$	$K = K_S \cdot K_F$	Toluene Insolubles (Coke) ^a
5	Redwater, B.C.				
	Original	1.7	3.3	5.6	<0.01
	Pyrolyzed				
	60 min.	1.2	1.7	2.0	0.2
10	90 min.	1.1	1.2	1.3	2.9
	CA Coastal				
	Original	1.3	2.6	3.4	<0.01
	Pyrolyzed				
	60 min.	1.0	b	-	4.4
15	90 min.	1.1	b	-	7.9
	Boscan				
	Original	1.7	3.2	5.4	<0.01
	Pyrolyzed				
	60 min.	1.1	1.3	1.4	7.5
20	90 min.	1.0	1.4	1.4	11.2
	MaxCL				
	Original	1.8	3.1	5.6	<0.01
	Pyrolyzed				
	90 min	1.0	1.2	1.2	7.0
25	Vistar				
	Original	1.6	2.6	4.2	<0.01
	Pyrolyzed				
	90 min.	-	-	-	-

90 min.

1.0

b

-

6.2

-
- a. Weight percent of toluene soluble material
 - b. Heithaus titration not possible due to multi phase product

5 It becomes apparent upon review of the plotted data, that a hydrocarbon material may have sufficient association between components to manifest unimodal characteristics such as a size ratio of the core material to the solvated core material (K_s) when K_s has a value equal to or greater than about 1.1, or a size ratio of a plurality of solvated core materials to other associated solvent (K_F) when K_F has a value equal to or greater than
10 about 1.4, or a sufficient solvation shell (K) when K has a value equal to or greater than about 1.5. For example, hydrocarbon materials having unimodal characteristics may comprise an amount of asphaltenes having polarity, an amount of solvents having lower polarity than the asphaltenes, and a sufficient amount of resins having a polarity intermediate to the polarity of the asphaltenes and the lower polarity of the solvents to
15 establish a solvation shell (K)= $(K_s \cdot K_F)$ at a value equal to or greater than about 1.5. These ascertainable measures of the unimodal characteristics of hydrocarbons with respect to K_s , K_F , and K constitute important embodiments of the invention.

As can easily understood, K_s , K_F , and K for a particular hydrocarbon material may be as indicia of stability for the unimodal characteristics of a hydrocarbon material. A first
20 indicia of stability may comprise determining an average size ratio of the solvated core material to the core material itself (indicia of stability $_{K_s}$), or determining an average size ratio of associated solvent around a plurality of solvated core materials to the core material itself (indicia of stability $_{K_F}$), or determining a size ratio of the associated solvent and solvation shell to the core material itself (indicia of stability $_K$). Naturally, these
25 relationships could be expressed in other terms or by the use of other devices and still provide effective indicia of stability.

Naturally, these size ratios may be determined using a variety of instruments such as a nuclear magnetic resonance spectroscopy device, a nuclear magnetic resonance tomography device, a mass spectrometry device, an infrared spectrometry device, a polaroscope device, a raman spectrometry device, a size exclusion chromatograph device, a gel electrophoresis device, or a paper chromatography device. The size ratios

may be determined prior to processing of the hydrocarbon material or during processing of the hydrocarbon material. For example, nuclear magnetic resonance imaging has shown that at least two distinct phases are present after pyrolysis with subsequent coke formation.

5 It can be further understood that establishing a threshold of instability for unimodal characteristics of hydrocarbon materials may comprise assigning a threshold of instability to size ratios having a value of K_s at about 1.1, or K_F at about 1.4, or K at about 1.5. Below these values the level of association between components in a hydrocarbon material may be insufficient to exhibit unimodal character and transition to
10 multimodal character may be initiated including heterogenous mixture formation, carbon deposition, or coke formation. Importantly, various embodiments of the invention allow for comparison of determined indicia of stability to the determined thresholds of instability with respect to K_s , K_F , or K so that the proximity of a particular hydrocarbon material to formation of multimodal characteristics. This may comprise comparing the
15 value of K_s for a given hydrocarbon material to the threshold of instability value of K_s . Similarly, the value of K_F for a given hydrocarbon material to the threshold of instability value of K_F , or the value of K for a given hydrocarbon material to the threshold of instability value of K . An approach which was not used prior to the instant invention.

Another embodiment of the invention can be based upon the free solvent volume of
20 the hydrocarbon material. The free solvent volume of hydrocarbon materials having unimodal character relates to the fraction of the total solvent that is not associated with the core materials or associated with or trapped by a plurality of solvated core materials. This indicia of stability can correlate with the amount of initial carbonaceous deposition, including coke formation, below pyrolysis temperatures or the initial amount of
25 carbonaceous deposition formed in the early stages of a pyrolytic process. This indicia of stability does not include the amount of carbonaceous deposition when pyrolysis is carried to completion. The total amount of carbonaceous deposition, including deposition of coke, may be estimated by further determining the hydrogen-carbon ratio of the hydrocarbon material. This ratio is subsequently used to calculate the weight of
30 the total carbon content of an amount of hydrocarbon material as would be well known to those with skill in the art. With respect to free solvent volume (ϕ_f), one manner of determining ϕ_{fs} comprises $\phi_{fs} = (1 - K_s(1 - p_d)(\alpha_d + 1.2))_f$. The average K_s for

unpyrolyzed hydrocarbon material value can be about 1.6. Values for ϕ_{FS} correlate to deposition of carbonaceous material when the value for K_s is held constant. Thus the only measurements which may be required to determine $\phi_{FS} = [1 - K_s (1/1 - p_a) (\chi_a/1.2)]$ in this manner can be the value of weight percent heptane asphaltenes (χ_a) and the value of
 5 petizabiltiy of asphaltenes (p_a). Other methods of determining free solvent volume, or modifying the values relating structure consideration such as H/C ratio, or fraction of bridge head aromatic carbons may be used, and are encompassed by the invention.

Regarding this embodiment of the invention, the weight percent heptane asphaltenes (χ_a), and the value of petizabiltiy of asphaltenes (p_a) may be determined as discussed
 10 above. Keeping in mind that the concept can work with other precipitating solvents and other dissolvents as discussed.

The p_a , χ_a , and the ϕ_{FS} for five hydrocarbon materials having unimodal characteristics were determined. The data for these determinations was compiled and provided in Table
 10.

15 Table 10. Free Solvent Volumes at 25°C

Residuum	$\chi/1.2$	p_a	ϕ_{ps}^a
Redwater, B.C.	0.097	0.698	0.49
CA Coastal	0.164	.0614	0.32
Boscan	0.165	0.691	0.14
20 MaxCL	0.151	0.682	0.24
Vistar	0.150	0.616	0.38

a. $K_s=1.6$

The five hydrocarbon materials were pyrolyzed in five (5) gram reactor tubes at 400°C for 90 minutes. The initial amount of carbonaceous deposition,
 25 including coke deposition, is set out for each hydrocarbon material in Table 11.

Table 11 Initial Coke Make in Tube Reactor for 90 Minutes at 400°C

	Residuum	Toluene Insolubles (Coke), Wt. %
	Redwater, B.C.	1.3
	CA Coastal	7.2
	Boscan	10.6
5	MaxCL	8.4
	Vistar	4.3

Now referring to Figure 13, which is a plot of initial deposition of carbonaceous material versus ϕ_{FS} . As can be understood, from the plot as ϕ_{FS} decreases the amount of initial carbonaceous material that forms increases for a given set of processing parameters. As such, an embodiment of the invention provides an indica of stability based upon ϕ_{FS} with respect to predicting the amount of initial carbonaceous deposition. Moreover, plots of initial carbonaceous material formation versus ϕ_{FS} could be generated for any variety of hydrocarbon materials for particular processing conditions, such as different pyrolysis temperatures or for different pyrolysis times or in various combinations, to rank the hydrocarbon materials in terms of relative carbon deposition potential based upon ϕ_{FS} .

As can be further understood additional embodiments of the invention may include selecting distillation parameters to distill hydrocarbon material having unimodal characteristics use predetermined indicia of stability to avoid reaching the threshold of instability. By distilling hydrocarbon material using distillation parameters that take into account or compare the indica of stability to the threshold of stability, prior to or during the distillation process or other processing event, it may be possible to select distillation parameters to allow substantially continuous distillation avoiding the threshold of instability for said unimodal characteristics. Specifically, selecting distillation parameters having predetermined indicia of stability may avoid or limit coke formation. Importantly, a method of processing hydrocarbon material using distillation parameters based upon indicia of stability, indicia of instability, independently or in cooperation, may allow distillation of hydrocarbon materials so as to have ascertainable indicia of stability in closer proximity to the threshold of instability compared to typical distillation parameters. By processing a hydrocarbon material so that the indicia of stability are closer to the threshold of instability in a substantially continuous distillation event, the

output of liquid distillables per unit amount of said hydrocarbon material may be increased by comparison with typical parameters of distillation. As described above, an increase in the amount of liquid distillables from the same amount of hydrocarbon material may decrease the amount of energy used per unit of liquid distillate produced, or
5 may also reduce the amount of emissions generated per unit of liquid distillate produced. Such reduction in emissions may be a reduction in carbon dioxide. Moreover, when hydrocarbon materials are distilled in a continuous distillation event it may increase the purity of at least a portion of said liquid distillates.

Another embodiment of the invention, understandably includes, the selection of
10 hydrocarbon materials for purchase or processing based upon determined indicia of stability for the degree of unimodal characteristics. Naturally, some hydrocarbon materials which have indicia of stability which show a high level of unimodal characteristics may have greater desirability for some parameters of processing. Alternately, with respect to some embodiments of the invention selecting distillation
15 parameters for hydrocarbon material having unimodal characteristics may be designed to reach a predetermined level of instability characteristics. As such, distilling these hydrocarbon materials using such distillation parameters may continue until reaching said predetermined level of instability characteristics. A method of processing hydrocarbon material in this fashion initiate the formation of a predetermined amount of
20 carbon or coke. Again as above, such distillation parameters may allow for maintaining continuous distillation until reaching the predetermined level of instability characteristics.

Naturally, because products from these processes may be distinguished from conventional processing by their purity an embodiment of the invention comprises the
25 isolation of these higher purity products.

As mentioned earlier, this invention can be embodied in a variety of ways. In addition, each of the various elements of the invention and claims may also be achieved in a variety of manners. This disclosure should be understood to encompass each such variation, be it a variation of an embodiment of any apparatus embodiment, a method or
30 process embodiment, or even merely a variation of any element of these. Particularly, it should be understood that as the disclosure relates to elements of the invention, the words for each element may be expressed by equivalent apparatus terms or method terms

-- even if only the function or result is the same. Such equivalent, broader, or even more generic terms should be considered to be encompassed in the description of each element or action. Such terms can be substituted where desired to make explicit the implicitly broad coverage to which this invention is entitled. As but one example, it should be understood that all action may be expressed as a means for taking that action or as an element which causes that action. Similarly, each physical element disclosed should be understood to encompass a disclosure of the action which that physical element facilitates. Regarding this last aspect, as but one example, the disclosure of a "dissolvent" should be understood to encompass disclosure of the act of "dissolving" -- whether explicitly discussed or not -- and, conversely, were there only disclosure of the act of "dissolving", such a disclosure should be understood to encompass disclosure of a "dissolvent." Such changes and alternative terms are to be understood to be explicitly included in the description.

The foregoing discussion and the claims which follow describe the preferred embodiments of the invention. Particularly with respect to the claims it should be understood that changes may be made without departing from their essence. In this regard it is intended that such changes would still fall within the scope of the present invention. It is simply not practical to describe and claim all possible revisions which may be accomplished to the present invention. To the extent such revisions utilize the essence of the invention each would naturally fall within the breadth of protection accomplished by this patent. This is particularly true for the present invention since its basic concepts and understandings are fundamental in nature and can be applied in a variety of ways to a variety of fields.

Any references mentioned, including but not limited to federal or state statutes, patents, publications, brochures, marketing materials, or inter-net pages, in this patent application, are hereby incorporated by reference or should be considered as additional text or as an additional exhibits or attachments to this application to the extent permitted; however, to the extent statements might be considered inconsistent with the patenting of this/these invention(s) such statements are expressly not to be considered as made by the applicant. Further, the disclosure should be understood to include support for each feature, component, and step shown as separate and independent elements and in various combinations and permutations of each.

In addition, unless the context requires otherwise, it should be understood that the term "comprise" or variations such as "comprises" or "comprising", are intended to imply the inclusion of a stated element or step or group of elements or steps but not the exclusion of any other element or step or group of elements or steps. Such terms should

5 be interpreted in their most expansive form so as to afford the applicant the broadest coverage legally permissible in countries such as Australia and the like. Such terms are intended to have an inclusive meaning rather than an exclusive one and should be interpreted in their most expansive form so as to afford the applicant the broadest coverage legally permissible. Therefore, in countries such as Australia and the like, such

10 terms are not intended to have an exclusive, or more limited meaning. Thus, the applicant should be understood to claim at least: i) a molecular weight / polarity map system; ii) each of the coking indexes; iii) a system of pre-distillation evaluation of hydrocarbon material; iv) a nearly continuous distillation system; v) a system for optimizing the yields of distillable liquids; vi) a system for determining the coking indexes; vii) the resulting

15 products; viii) the related methods disclosed and described, ix) similar, equivalent, and even implicit variations of each of these devices and methods; x) those alternative designs which accomplish each of the functions shown as are disclosed and described; xi) those alternative designs and methods which accomplish each of the functions shown as are implicit to accomplish that which is disclosed and described; xii) each feature,

20 component, device, and step shown as separate and independent inventions; xiii) the combinations of applied systems including the designs disclosed, xiv) the resulting products produced by such systems or components, xv) related methods including the techniques of the applied systems, and xvi) the various combinations and permutations of each of the above.

VI. CLAIMS

We claim:

1. A molecular weight - polarity map for hydrocarbon materials having unimodal characteristics comprising:
 - 5 a. a first axis having values relating to molecular weight;
 - b. a second axis having values relating to solubility parameter;
 - c. a plurality of solvent tuned contour lines each defining a solubility parameter range in $(\text{cal/cc})^{1/2}$; and
 - d. a core material solubility region.
- 10 2. A molecular weight - polarity map for hydrocarbon materials as described in claim 1, wherein said core material solubility region comprises between about $6.9 (\text{cal/cc})^{1/2}$ to about $11.0 (\text{cal/cc})^{1/2}$.
3. A molecular weight - polarity map for hydrocarbon materials as described in claim 1, wherein said solubility parameter range in $(\text{cal/cc})^{1/2}$ comprises about 0.5 to about 0.6
- 15 $(\text{cal/cc})^{1/2}$.
4. A molecular weight - polarity map for hydrocarbon materials as described by claim 1, wherein said core material comprises asphaltenes.
5. A molecular weight - polarity map for hydrocarbon materials as described by claim 1, wherein a first solvent tuned contour line comprises an iso-octane tuned contour line.
- 20 6. A molecular weight - polarity map for hydrocarbon materials as described by claim 5, wherein a second solvent tuned contour line comprises a heptane tuned contour line.
7. A molecular weight - polarity map for hydrocarbon materials as described by claim 6, wherein a third solvent tuned contour line comprises a heptane:toulene (2:1) (v:v) tuned

8. A molecular weight - polarity map for hydrocarbon materials as described by claim 7, wherein a fourth solvent tuned contour line comprises a heptane:toulene (1:2) (v:v) tuned contour line.
9. A molecular weight - polarity map for hydrocarbon materials as described by claim 8,
5 wherein a fifth solvent tuned contour line comprises a toulene tuned contour line.
10. A molecular weight - polarity map for hydrocarbon materials as described by claim 9, wherein a sixth solvent tuned contour line comprises a toluene:carbon disulfide (55:45) (v:v) tuned contour line.
11. A molecular weight - polarity map for hydrocarbon materials as described by claim
10 10, wherein a seventh solvent tuned contour line comprises a carbon disulfide tuned contour line.
12. A molecular weight - polarity map for hydrocarbon materials as described by claim 1, further comprising molecular weight - polarity coordinate locations of said core materials.
- 15 13. A molecular weight - polarity map for hydrocarbon materials as described by claim 12, wherein said molecular weight - polarity coordinate locations of said core materials relate to at least one unimodal characteristic.
14. A molecular weight - polarity map for hydrocarbon materials as described by claim 13, wherein said at least one unimodal characteristic comprises a variably adjustable core
20 material having a molecular weight responsive to temperature change.
15. A molecular weight - polarity map for hydrocarbon materials as described by claim 13, wherein said at least one unimodal characteristic comprises a core material having a polarity stabilizer function responsive to temperature change.
16. A molecular weight - polarity map for hydrocarbon materials as described by claim

14, wherein variably adjustable core material comprises a core material that decreases in molecular weight in response to an increase in temperature.

17. A method of processing hydrocarbon material, comprising the steps of:

- a. providing an amount of said hydrocarbon material having at least one unimodal
5 characteristic; and
- b. determining at least one indicia of stability based on said at least one unimodal characteristic.

18. A method of processing hydrocarbon material as described in claim 17, further comprising the steps of:

- 10 a. establishing at least one threshold of instability of said at least one unimodal characteristic;
- b. comparing said at least one indicia of stability to said at least one threshold of instability; and
- c. assessing the proximity of said at least one unimodal characteristic to forming a
15 multimodal characteristic.

19. A method of processing hydrocarbon material as described in claim 17, wherein having said at least one unimodal characteristic comprises ascertaining an average size ratio of a solvated core material size to a core material size (K_s), wherein K_s has a value equal to or greater than about 1.1.

20

20. A method of processing hydrocarbon material as described in claim 17, wherein having said at least one unimodal characteristic comprises ascertaining an average size ratio of solvent associated with a plurality of solvated core materials to said plurality of solvated core materials (K_F), wherein K_F has a value equal to or greater than about 1.4.

25

21. A method of processing hydrocarbon material as described in claim 17, wherein having said at least one unimodal characteristic comprises ascertaining a solvation shell R_s , wherein $R_s = (K_s - 1) \times R_c$ and a value equal to or greater than about 1.

22. A method of processing hydrocarbon material as described in claim 17, wherein having said at least one unimodal characteristic comprises:
- a. maintaining an amount of asphaltenes having polarity;
 - b. maintaining an amount of solvents having lower polarity than said asphaltenes; and
 - 5 c. maintaining a sufficient amount of resins having a polarity intermediate to said polarity of said asphaltenes and to said lower polarity of said solvents to establish a value of said solvation shell (K) = ($K_s \cdot K_F$) equal to or greater than about 1.5.
23. A method of processing hydrocarbon material as described in claim 17, wherein said step of providing an amount of hydrocarbon material further comprises the step of
- 10 selecting said hydrocarbon material from the group consisting of coal tars, shale oils, tar sand bitumen, asphalts, heavy oils, and petroleum residua.
24. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining at least one indicia of stability based on said at least one unimodal characteristic comprises determining a value of K_s of said hydrocarbon
- 15 material, wherein $K_s = K_s = (1/(1-\chi_{cy}))$.
25. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining at least one indicia of stability based on said at least one unimodal characteristic comprises determining a value of K_F of said hydrocarbon material, wherein $K_F = K_F = (1/(1-p_a))$.
- 20 26. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining at least one indicia of stability based on said at least one unimodal characteristic comprises determining a value of K of said hydrocarbon material, wherein $K = K_s \cdot K_F$, and wherein $K_s = K_s = (1/(1-\chi_{cy}))$, and wherein $K_F = K_F = (1/(1-p_a))$.
- 25 27. A method of processing hydrocarbon material as described in claim 24, wherein determining said at least one indicia of stability for said unimodal characteristic comprises determining said value of K_s of said hydrocarbon material using nuclear magnetic

resonance, wherein absorption of electromagnetic radiation by said solvated core material and absorption of electromagnetic radiation by said core material are analyzed to ascertain said average size ratio K_s .

28. A method of processing hydrocarbon material as described in claim 25, wherein
5 determining at least one indicia of stability for said unimodal characteristics comprises determining said value of K_F of said hydrocarbon material using nuclear magnetic resonance, wherein absorption of electromagnetic radiation by said solvent associated with said solvated core materials and absorption of electromagnetic radiation by said plurality of solvated core materials are analyzed to ascertain said average size ratio K_F .
- 10 29. A method of processing hydrocarbon material as described in claim 26, wherein determining at least one indicia of stability for said unimodal characteristics comprises determining a value of $K = K_s \cdot K_F$ of said hydrocarbon material using magnetic resonance, wherein absorption of electromagnetic radiation by said solvated core material and absorption of electromagnetic radiation by said core material are analyzed to
15 ascertain said average size ratio K_s , and wherein absorption of electromagnetic radiation by said solvent associated with said solvated core materials and absorption of electromagnetic radiation by said plurality of solvated core materials are analyzed to provide said average size ratio K_F .
30. A method of processing hydrocarbon material as described in claim 18, wherein
20 establishing a threshold of instability based on said at least one unimodal characteristics comprises assigning a value of about 1.1 to a threshold of instability K_s .
31. A method of processing hydrocarbon material as described in claim 18, wherein establishing a threshold of instability based on said at least one unimodal characteristic comprises assigning a value of about 1.4 to a threshold of instability K_F .
- 25 32. A method of processing hydrocarbon material as described in claim 18, wherein establishing a threshold of instability based on said unimodal characteristics comprises assigning a value of about 1.2 to a threshold of instability K .

33. A method of processing hydrocarbon material as described in claim 18, wherein said step of comparing said indicia of stability to said threshold of instability comprises comparing a determined value of K_s of said hydrocarbon material to said value of about 1.1 assigned to said threshold of instability K_s .
- 5 34. A method of processing hydrocarbon material as described in claim 18, wherein said step of comparing said indicia of stability to said threshold of instability comprises comparing a determined value of K_F of said hydrocarbon material to said value of about 1.4 assigned to said threshold of instability K_F .
35. A method of processing hydrocarbon material as described in claim 18, wherein
10 said step of comparing said indicia of stability to said threshold of instability comprises comparing a determined value of K of said amount of said hydrocarbon material to said value of about 1.5 assigned to said threshold of instability K .
36. A method of processing hydrocarbon material as described in claims 19, 20, 21, 24,
25, 26, 27, 28, or 29, further comprising the step of using a hydrocarbon material
15 analysis device to determine said size ratio selected from the group consisting of a nuclear magnetic resonance device, a nuclear magnetic resonance spectroscopy device, a nuclear magnetic resonance tomography device, a mass spectrometry device, an infrared spectrometry device, a raman spectroscopy device, a size exclusion chromatography device, a gel electrophoresis device, and paper chromatography device.
- 20 37. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining indicia of stability for said unimodal characteristics comprises:
a. providing a hydrocarbon material component analysis device;
b. calibrating said hydrocarbon material component analysis device;
c. mixing an amount of hydrocarbon material in a precipitating solvent;
25 d. precipitating asphaltenes from said hydrocarbon material;
e. extracting maltenes into said precipitating solvent;
f. combining maltenes with said hydrocarbon material component analysis device;
g. determining an amount of at least one unimodal characteristic stability component in

said maltenes.

38. A method of processing hydrocarbon material as described in claim 37, wherein said step of providing a hydrocarbon material component analysis device comprises selecting said hydrocarbon material component analysis device from the group consisting of a nuclear magnetic resonance spectroscopy device, a nuclear magnetic resonance tomography device, a mass spectrometry device, an infrared spectrometry device, a microscope device, an infrared raman spectroscopy device, a size exclusion chromatography device, a gel electrophoresis device, and a paper chromatograph device.
39. A method of processing hydrocarbon material as described in claim 37, wherein said step of calibrating said hydrocarbon material component analysis device comprises identifying characteristics of polystyrene having known molecular weight.
40. A method of processing hydrocarbon material as described in claim 39, wherein said precipitating solvent comprises iso-octane.
41. A method of processing hydrocarbon material as described in claim 40, wherein said step of analyzing said maltenes with said hydrocarbon material component analysis device comprises:
- separating said maltenes with said size exclusion chromatography device; and
 - comparing elution volumes of said maltenes to elution volumes of said components of polystyrene having known molecular weight.
42. A method of processing hydrocarbon material as described in claim 41, wherein determining an amount of said at least one unimodal characteristic stability component in said maltenes comprises detecting an apparent molecular weight of said at least one unimodal characteristic stability component.
43. A method of processing hydrocarbon material as described in claim 42, wherein detecting the apparent molecular weight of said at least one unimodal characteristic stability component comprises observing elution of said at least one unimodal

characteristic stability component corresponding to a leading edge high molecular weight shoulder component.

44. A method of processing hydrocarbon material as described in claim 43, wherein said leading edge high molecular weight component has an apparent molecular weight
5 about equal to or greater than about 500 gram per mole.

45. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining indicia of stability based on said at least one unimodal characteristic comprises:

- a. providing a titration device;
- 10 b. mixing an amount of said hydrocarbon material into an amount of aromatic dissolvent (V_s);
- c. titrating dissolvent soluble components in said amount of aromatic dissolvent with an amount of weak aliphatic solvent until a flocculent forms (V_t);
- d. calculating the flocculation ratio at infinite dilution (FR_{max}), wherein $FR_{max} = V_s / (V_s$
15 $+ V_t)$, and wherein V_s has a value about equal to said volume of dissolvent, and wherein V_t has a value about equal to said amount of weak solvent;
- e. determining the dilution concentration at zero titrant level (C_{min}), wherein $C_{min} = W_a / (V_s + V_t)$, and wherein W_a has a value about equal to said amount of said hydrocarbon material;
- 20 f. determining the peptizability of asphaltenes determining (p_a), wherein $p_a = 1 - FR_{max}$; and
- g. determining a value of p_a / C_{min} for said amount of toluene soluble components.

46. A method of processing hydrocarbon material as described in claim 45, wherein said step of mixing an amount of said hydrocarbon material into an amount of aromatic
25 dissolvent (V_s) comprises mixing said amount of said hydrocarbon material into an amount of toluene.

47. A method of processing hydrocarbon material as described in claim 45, wherein said step of titrating dissolvent soluble components in said volume of aromatic dissolvent

with an amount of weak aliphatic solvent until a flocculent forms (V_f) comprises titrating said dissolvent soluble components in said volume of aromatic dissolvent with an amount of iso-octane.

48. A method of processing hydrocarbon material as described in claim 18, wherein
 5 said step of establishing a threshold of instability based on said at least one unimodal characteristic comprises assigning a value within the range of about 0.1 to about 0.4 to a threshold of instability p_a / C_{min} .

49. A method of processing hydrocarbon material as described in claim 48, wherein
 10 said step of comparing said indicia of stability to said threshold of instability comprises comparing said determined value of p_a / C_{min} of said hydrocarbon material to said value of about 0.1 to about 0.4 assigned to said threshold of instability p_a / C_{min} .

50. A method of processing hydrocarbon material as described in claim 17, wherein
 said step of determining indicia of stability based on said at least one unimodal characteristic comprises:
 15 a. precipitating an amount of asphaltene_x from an amount of said hydrocarbon material with a first solvent;
 b. extracting precipitated asphaltene_x with a second solvent, wherein said second solvent has a polarity between a polarity of said first solvent and a polarity of a third solvent capable of substantially dissolving said asphaltene_x completely; and
 20 c. determining an amount of asphaltene_y soluble in said second solvent.

51. A method of processing hydrocarbon material as described in claim 50, wherein
 said step of precipitating an amount of asphaltene_x from an amount of said hydrocarbon material with a first solvent further comprises the step of selecting said first solvent from the group consisting of iso-octane, pentane, hexane, and heptane.

25 52. A method of processing hydrocarbon material as described in claim 51, wherein
 said step of extracting precipitated asphaltene_x with a second solvent, wherein said second solvent has polarity between the polarity of said first solvent and a polarity of a

third solvent capable of substantially dissolving said asphaltenes_x completely further comprises the step of selecting said second solvent from the group consisting of cyclohexane, pentane, hexane, heptane, and heptane:toluene (1:1) (v:v).

53. A method of processing hydrocarbon material as described in claim 18, wherein
5 said step of establishing a threshold of instability based on said at least one unimodal characteristic comprises assigning a value of equal to or less than about 0.2 weight percent to a threshold of instability_y.

54. A method of processing hydrocarbon material as described in claim 18, wherein
said step of determining indicia of stability based on said at least one unimodal
10 characteristic comprises weight percent asphaltenes_y soluble in said second solvent over weight percent asphaltenes_x precipitated by said first solvent.

55. A method of processing hydrocarbon material as described in claim 2 wherein said
step of establishing a threshold of instability based on said at least one unimodal
characteristic comprises assigning a value between about 0.0 to about 1.0 to a threshold
15 of instability_{x/y}.

56. A method of processing hydrocarbon material as described in claims 18, 24, 34, 35,
42, 43, 44, 49, 53, or 54, further comprising the step of predicting the proximity of said
hydrocarbon material to coke formation.

57. A method of processing hydrocarbon material as described in claim 17, wherein
20 said step of determining indicia of stability based on said at least one unimodal characteristic comprises determining free solvent volume.

58. A method of processing hydrocarbon material as described in claim 57, wherein
determining said free solvent volume comprises determining an amount of unassociated
solvent in said hydrocarbon material, wherein said unassociated solvent does not solvate
said core material and wherein said unassociated solvent does not associate with said
plurality of solvated core materials.

59. A method of processing hydrocarbon material as described in claim 57, wherein determining said free solvent volume comprises determining $\phi_{FS} = 1 - K_s (1/1 - p_a) (\chi_a/1.2)$, wherein K_s has a value of about 1.6.

60. A method of processing hydrocarbon material as described in claim 56, wherein
- 5 determining said free solvent volume comprises:
 - a. providing a titration device;
 - b. mixing an amount of said hydrocarbon material into an amount of aromatic dissolvent (V_s);
 - c. titrating dissolvent soluble components in said amount of aromatic dissolvent with an
 - 10 amount of weak aliphatic solvent until a flocculent forms (V_l);
 - d. calculating the flocculation ratio at infinite dilution (FR_{max}), wherein $FR_{max} = V_s / (V_s + V_l)$, and wherein V_s has a value about equal to said amount of aromatic dissolvent, and wherein V_l has a value about equal to said amount of weak aliphatic solvent;
 - e. determining the peptizability of asphaltenes p_a , wherein $p_a = 1 - FR$;
 - 15 f. precipitating an amount of asphaltenes from an amount of said hydrocarbon material with a precipitating solvent;
 - g. determining the mass fraction asphaltenes (χ_a); and
 - h. determining ϕ_{FS} , wherein $\phi_{FS} = 1 - K_s (1/1 - p_a) (\chi_a/1.2)$.

61. A method of processing hydrocarbon material as described in claim 60, wherein

- 20 said step of mixing an amount of said hydrocarbon material into an amount of aromatic dissolvent (V_s) further comprises selecting said aromatic dissolvent from the group consisting of toluene, benzene, xylene, and ethylbenzene.

62. A method of processing hydrocarbon material as described in claim 60, wherein

- 25 said step of titrating dissolvent soluble components in said amount of aromatic dissolvent with an amount of weak aliphatic solvent until a flocculent forms (V_l) further comprises selecting said aliphatic solvent from the group consisting of iso-octane, pentane, hexane, and hexadecane.

63. A method of processing hydrocarbon material as described in claim 47 wherein

said step of precipitating an amount of asphaltenes from an amount of said hydrocarbon material with a precipitating solvent further comprises the step of selecting said precipitating solvent from the group consisting of iso-octane, pentane, hexane, and heptane.

5 64. A method of processing hydrocarbon material as described in claim 57, further comprising the step of determining an initial amount of coke formation when exceeding said threshold of instability .

65. A method of processing hydrocarbon material as described in claims 17, 18, 33, 34, 35, 37, 41, 44, 45, 46, 47, 49, 50, 53, 54, 55, 57, 59, 60, or 64, further comprising the
10 steps of:

- a. selecting distillation parameters to distill said hydrocarbon material having unimodal characteristics, wherein said distillation parameters have predetermined indicia of stability to avoid reaching said threshold of instability;
- b. distilling said hydrocarbon material using said distillation parameters; and
- 15 c. avoiding the threshold of instability for said unimodal characteristics.

66. A method of processing hydrocarbon material as described in claim 65, wherein said step of selecting distillation parameters to distill said hydrocarbon material having unimodal characteristics, wherein said distillation parameters have predetermined indicia
20 of stability to avoid reaching said threshold of instability comprises selecting distillation parameters having predetermined indicia of stability to avoid coke formation.

67. A method of processing hydrocarbon material as described in claim 61, further comprising the step of maintaining continuous distillation until reaching said predetermined indicia of stability to avoid coke formation.

25 68. A method of processing hydrocarbon material as described in claim 67, wherein said step of distilling said hydrocarbon material using said distillation parameters comprise the step of distilling said hydrocarbon materials so as to have indicia of stability in closer proximity to said threshold of instability compared to typical

distillation parameters.

69. A method of processing hydrocarbon material as described in claims 17, 18, 33, 34, 35, 37, 41, 44, 45, 46, 47, 49, 50, 53, 54, 55, 57, 59, 60, or 64 further comprising the steps of:

- 5 a. selecting distillation parameters for said hydrocarbon material having unimodal characteristics to reach a predetermined level of instability characteristics;
- b. distilling said hydrocarbon material using said distillation parameters; and
- c. continuing said hydrocarbon material until reaching said predetermined level of instability characteristics.

10 70. A method of processing hydrocarbon material as described in claim 69, wherein said step of reaching said predetermined level of instability comprises initiating a predetermined amount of coke.

71. A method of processing hydrocarbon material as described in claim 70, further comprising the step of maintaining continuous distillation until reaching said
15 predetermined level of instability characteristics.

72. A method of processing hydrocarbon material as described in claim 71, further comprising the step of determining the hydrogen-carbon ratio of said hydrocarbon material.

73. A method of processing hydrocarbon material as described in claim 72, further
20 comprising the step of determining a total amount of coke which may form from said hydrocarbon material.

74. A method of processing hydrocarbon material as described in claim 68, further comprising the step of increasing output of liquid distillate per unit amount of said hydrocarbon material.

75. A method of processing hydrocarbon material as described in claim 68, further:

comprising the step of decreasing the amount of energy used per unit of liquid distillate produced.

76. A method of processing hydrocarbon material as described in claim 68, further
5 comprising the step of reducing the amount of emissions generated per unit of liquid distillate produced.

77. A method of processing hydrocarbon material as described in claim 76, wherein said step of reducing the amount of emissions generated per unit of liquid distillate produced comprises reducing carbon dioxide emissions.

10 78. A method of processing hydrocarbon material as described in claim 68, further comprising the step of increasing the purity of at least a portion of said liquid distillates.

79. A method of processing hydrocarbon material as described in claim 17, 18, 33, 34, 35, 37, 41, 44, 45, 46, 47, 49, 50, 53, 54, 55, 57, 59, 60, or 64, further comprising the step of selecting said hydrocarbon material to process based upon said indica of stability
15 for said unimodal characteristics.

80. A method of processing hydrocarbon material as described in claim 36, further comprising the step of selecting said hydrocarbon material to process based upon said indica of stability for said unimodal characteristics.

81. Liquid distillate produced in accordance with the process of claim 65.

20 82. Liquid distillate produced in accordance with the process of claim 68.

83. Liquid distillate produced in accordance with the process of claim 69.

84. Liquid distillate produced in accordance with the process of claim 71.

85. A hydrocarbon material comprising.

- a. an amount of core material having polarity;
 - b. an amount of solvents having lower polarity than said core material; and
 - c. an amount of resins having a polarity intermediate to said polarity of said core material and to said lower polarity of said solvents sufficient to establish at least one
- 5 unimodal characteristic.

86. A hydrocarbon material as described in claim 85, wherein said at least one unimodal characteristic comprises a value of a solvation shell (K), and wherein $K = (K_s \cdot K_f)$ has a value equal to or greater than about 1.5.

87. A hydrocarbon material as described in claim 85, wherein said at least one unimodal
10 characteristic comprises a value of an average size ratio of a solvated core material size to a core material size (K_s), wherein K_s has a value equal to or greater than about 1.1.

88. A hydrocarbon material as described in claim 85, wherein said at least one unimodal characteristic comprises a value of an average size ratio of solvent associated with a
15 plurality of solvated core materials to said plurality of solvated core materials (K_f), wherein K_f has a value equal to or greater than about 1.4.

89. A hydrocarbon material as described in claim 85, wherein said core material comprises asphaltenes.

90. A hydrocarbon material as described in claim 85, wherein said hydrocarbon material
20 has an indicia of stability based on said at least one unimodal characteristic which has a value outside the range naturally occurring hydrocarbon materials.

91. A hydrocarbon material as described in claim 85, further comprising a level of purity greater than naturally occurring hydrocarbon materials.

92. Methods substantially as described hereinbefore and with reference to any of the accompanying examples.

93. Apparatuses substantially as described hereinbefore and with reference to any of the accompanying examples.

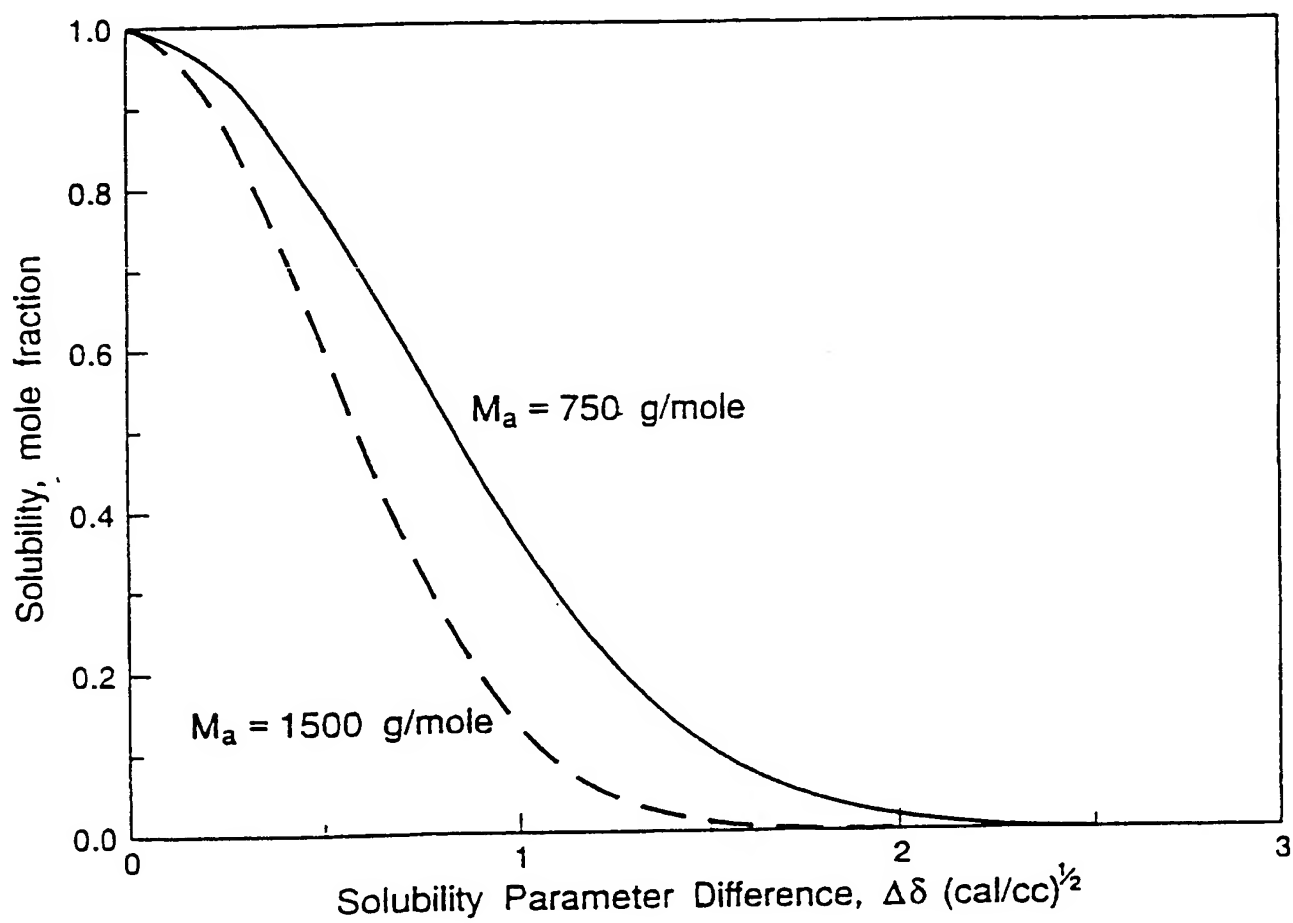


FIG. 1

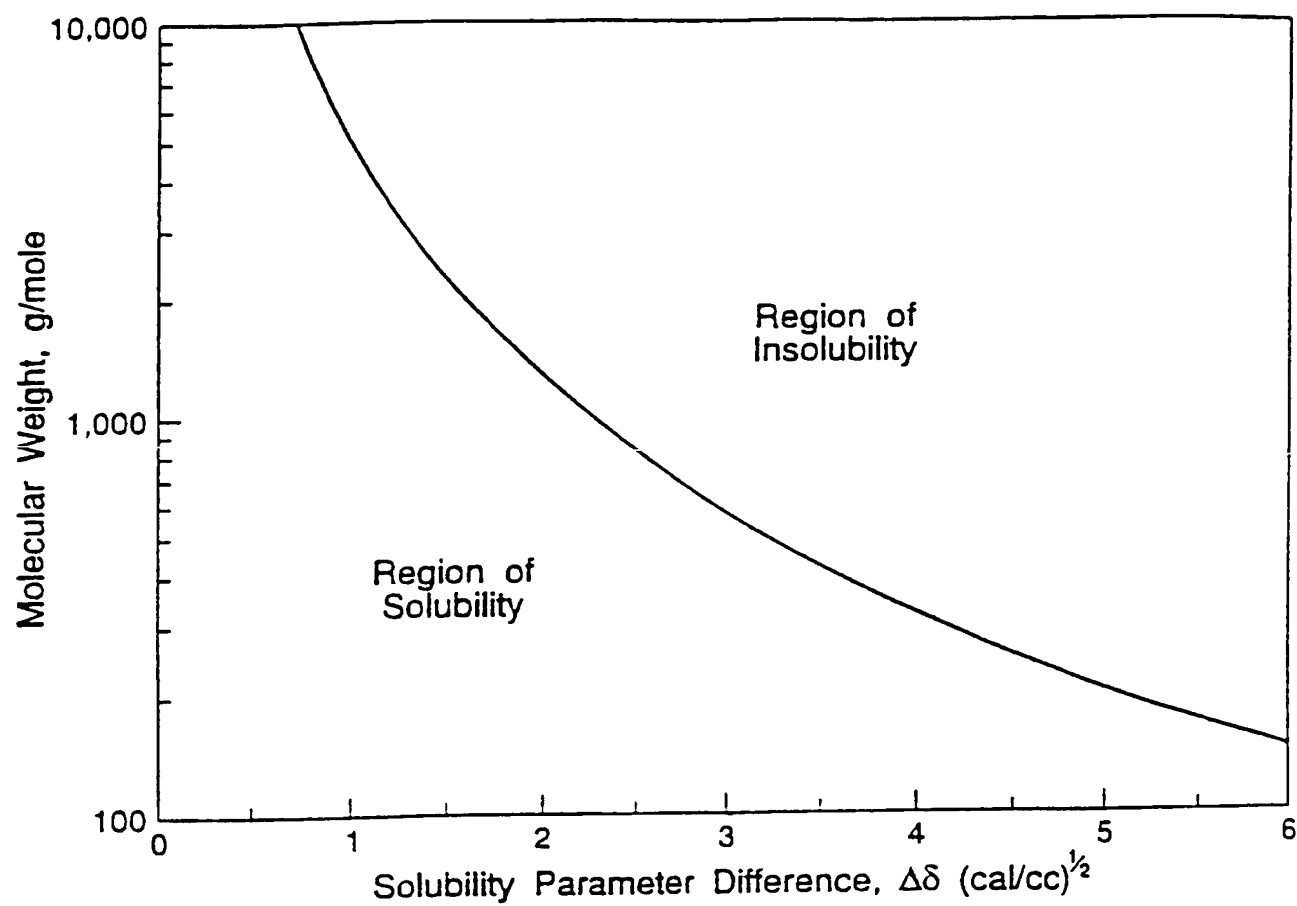


FIG. 2

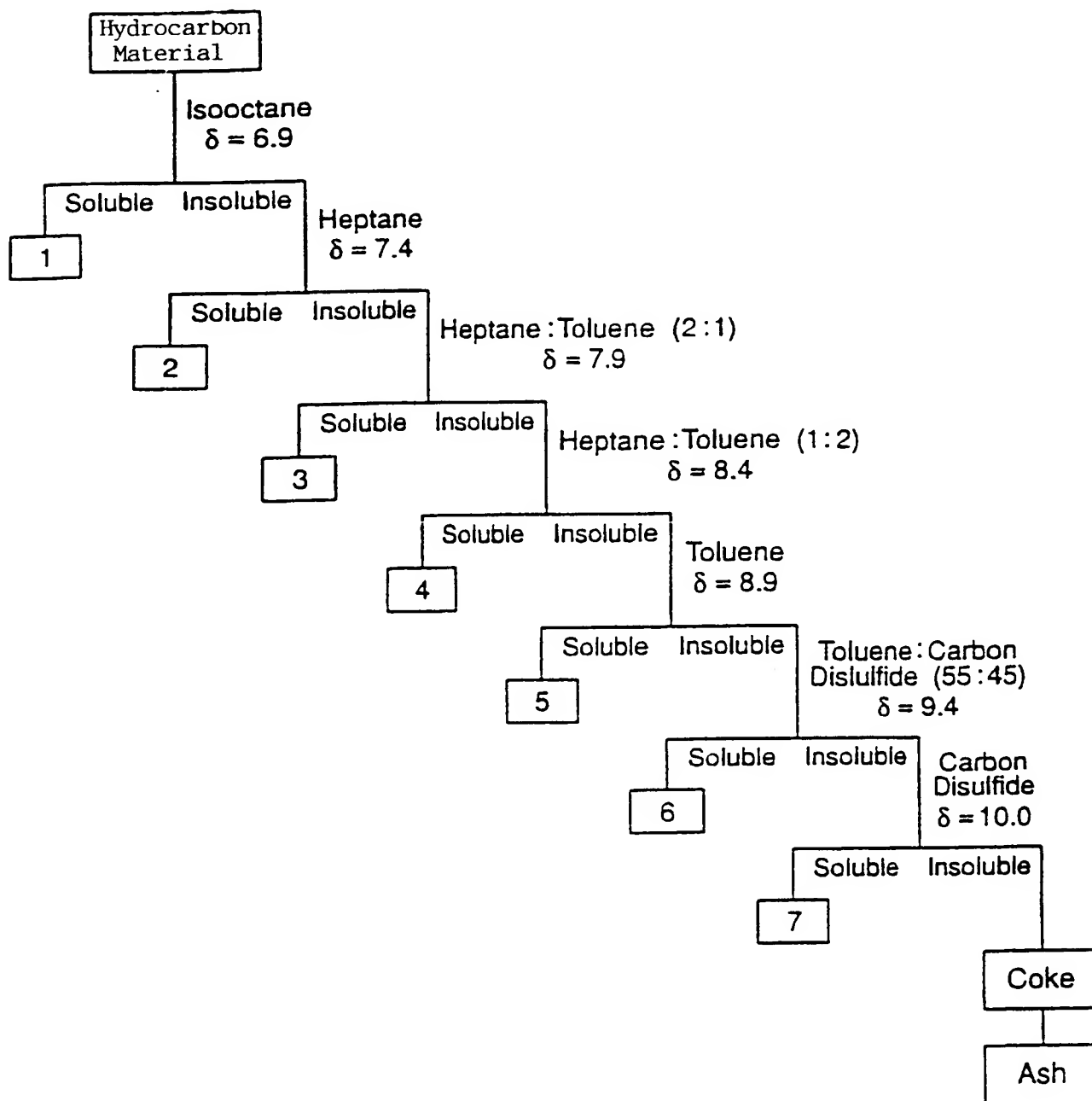


FIG. 3

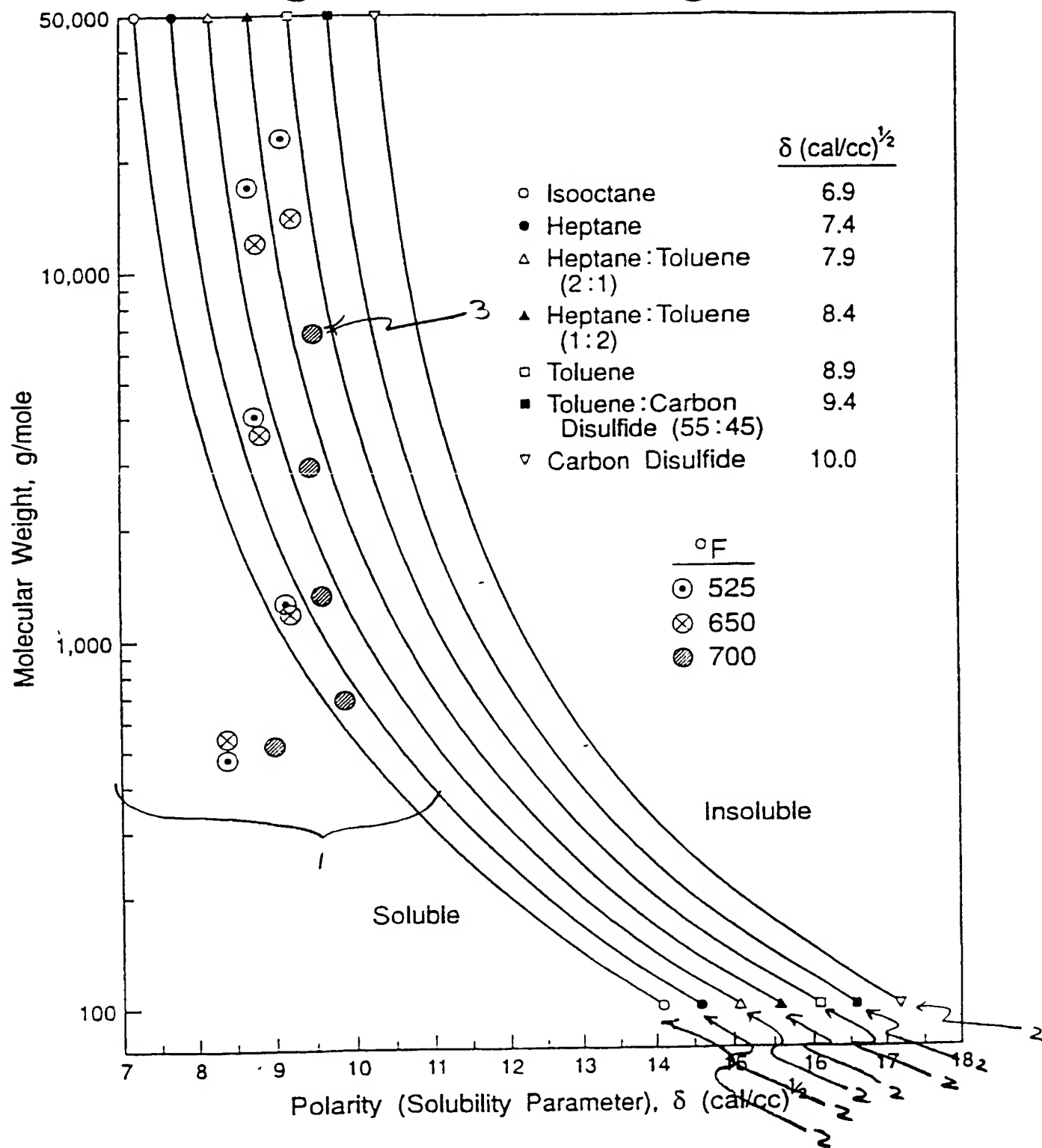


FIG. 4

Attenuated Reflective Index Detector Response

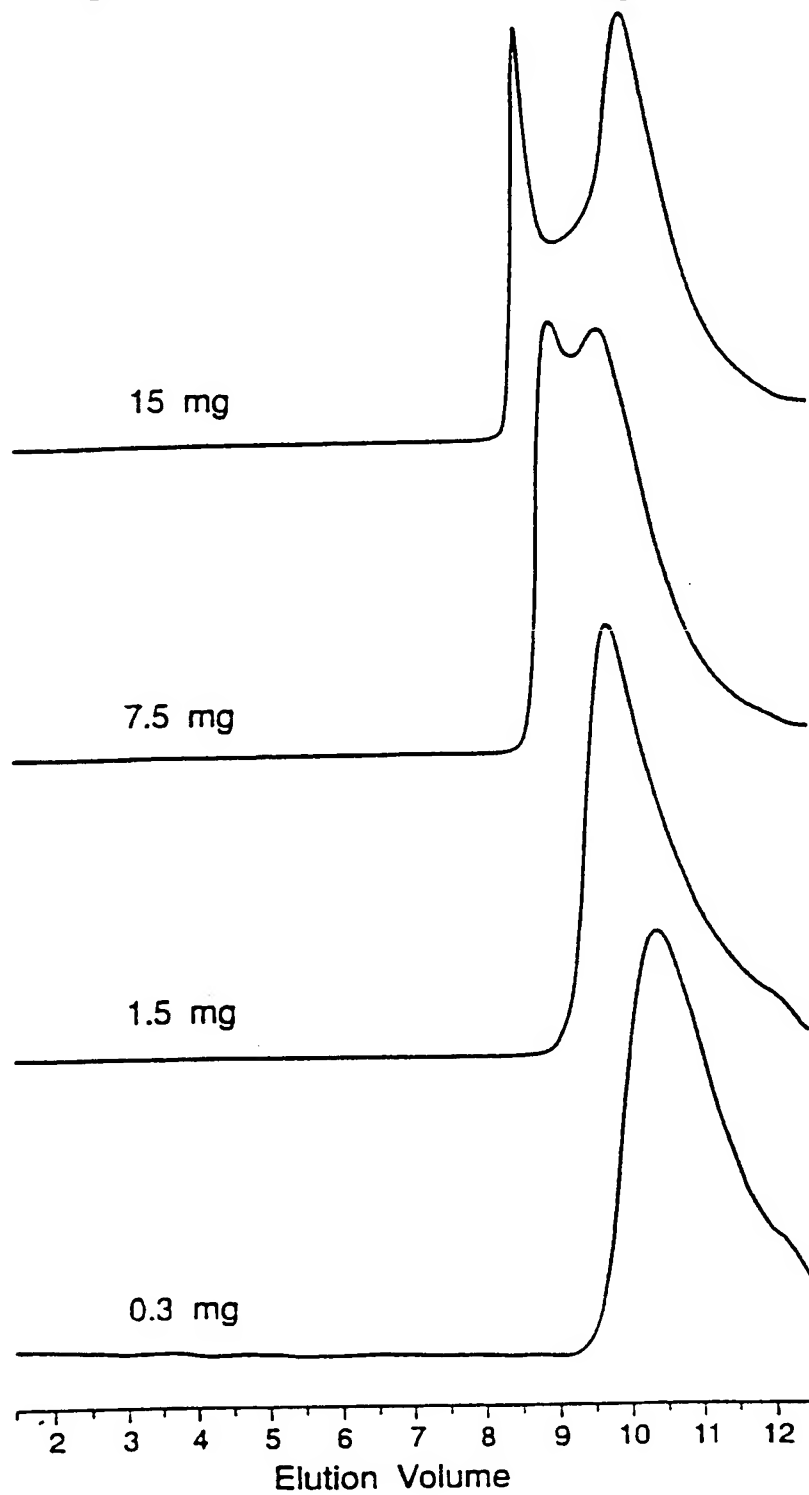


FIG. 5

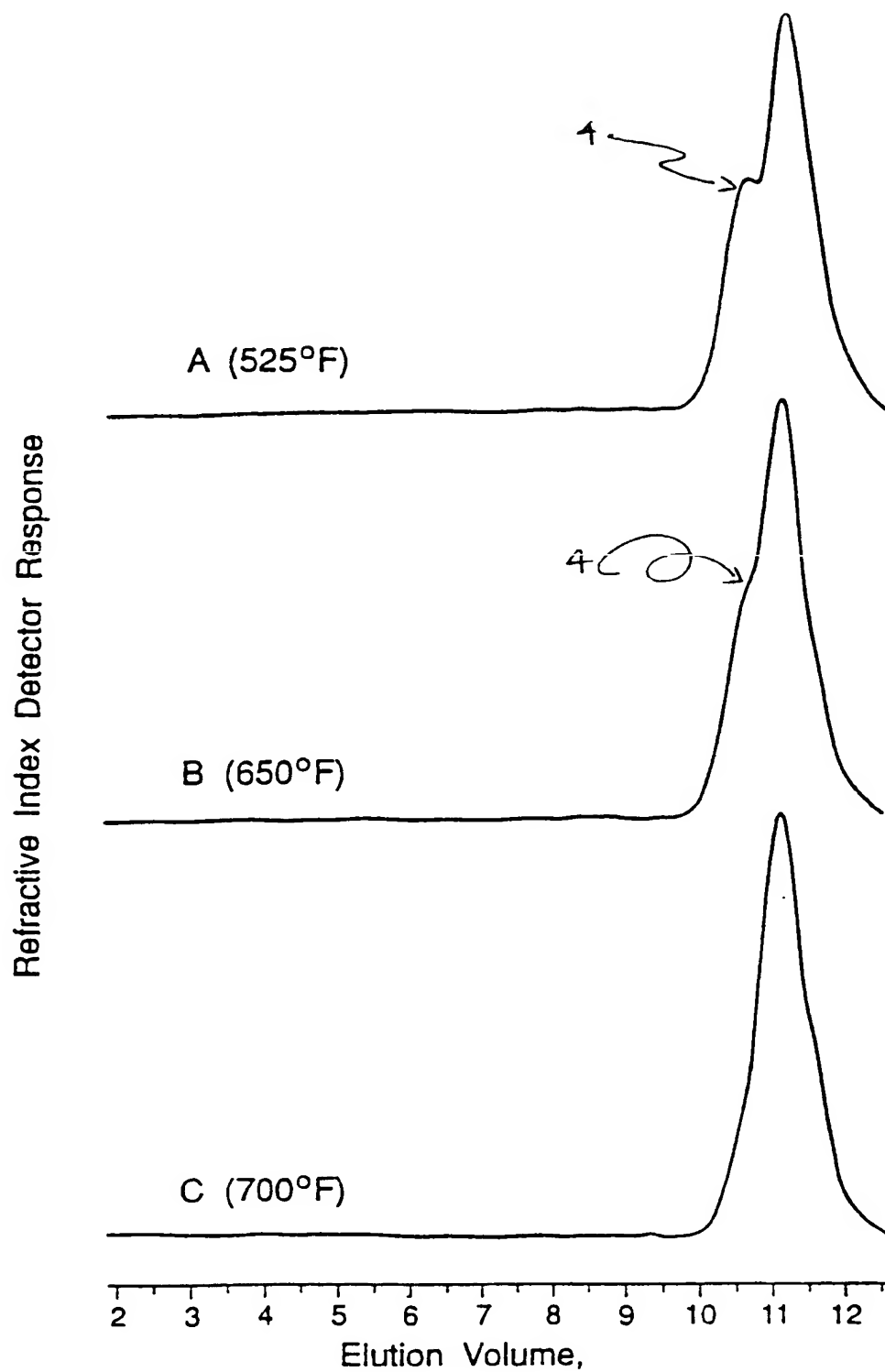


FIG. 6

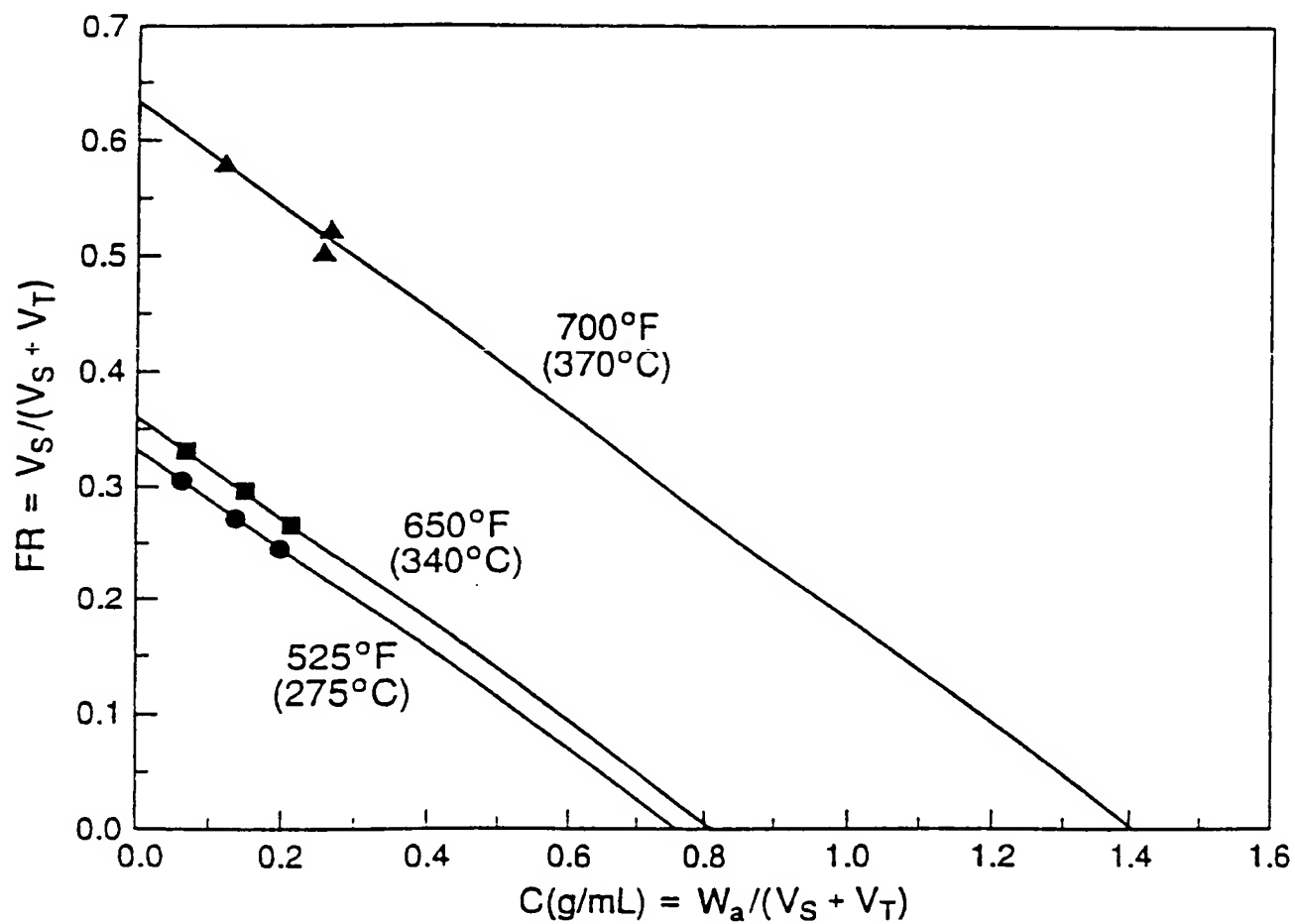


FIG. 7

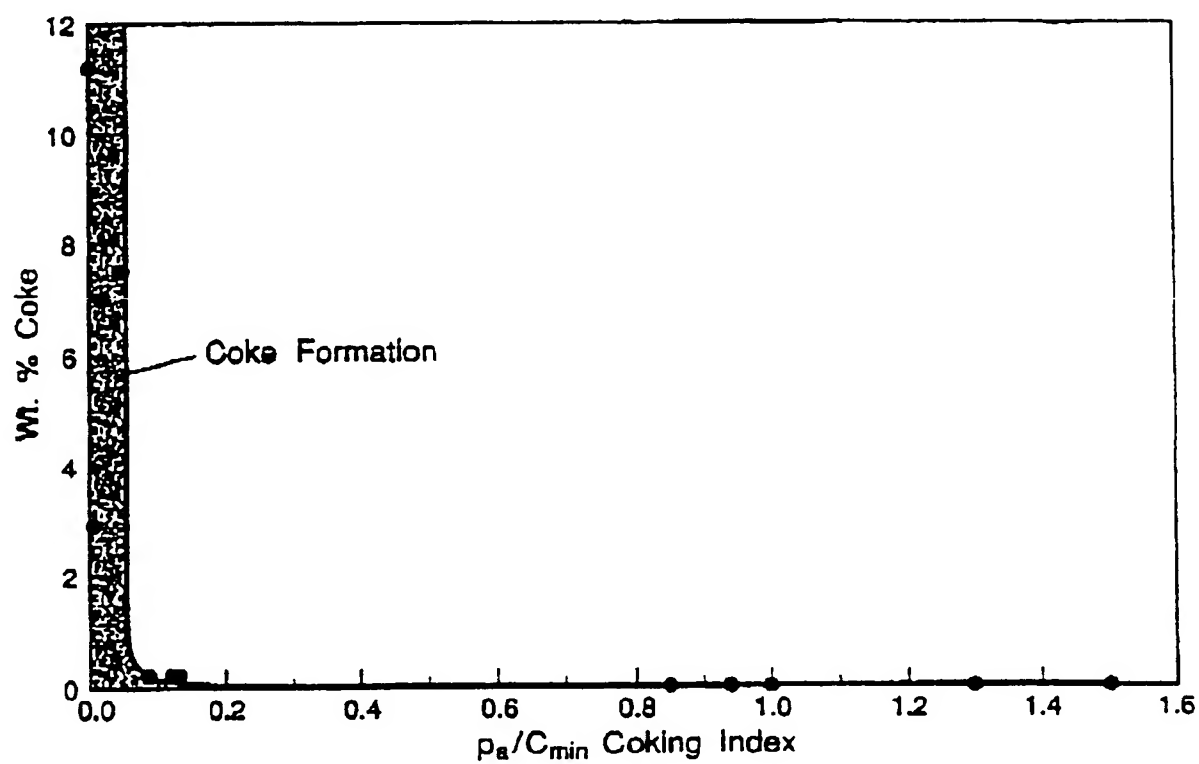


FIG. 8

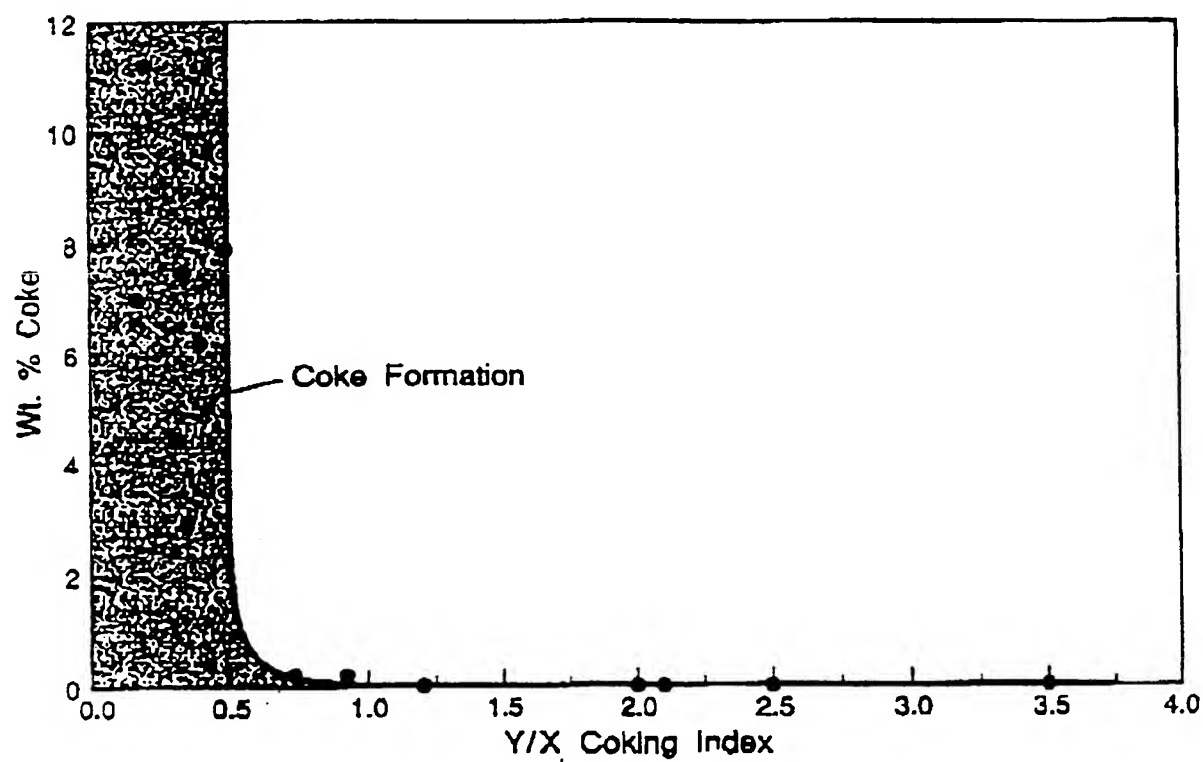


FIG. 9

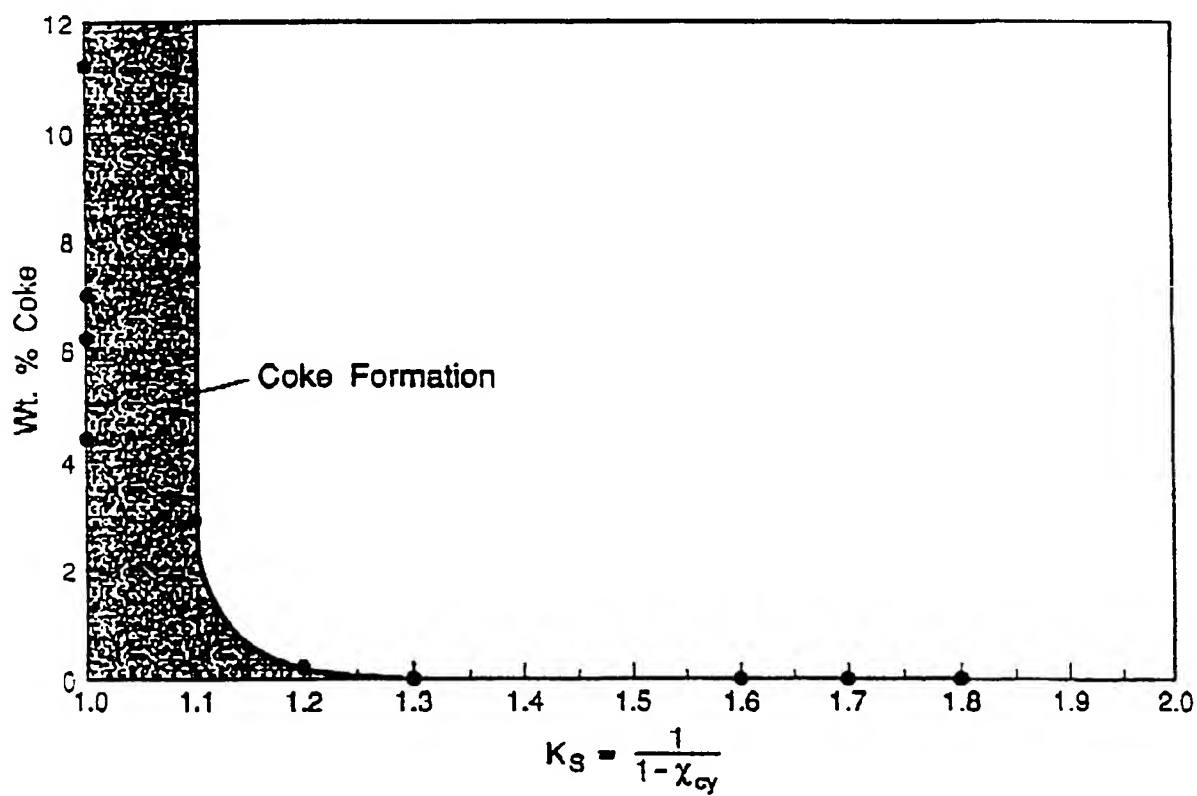


FIG. 10

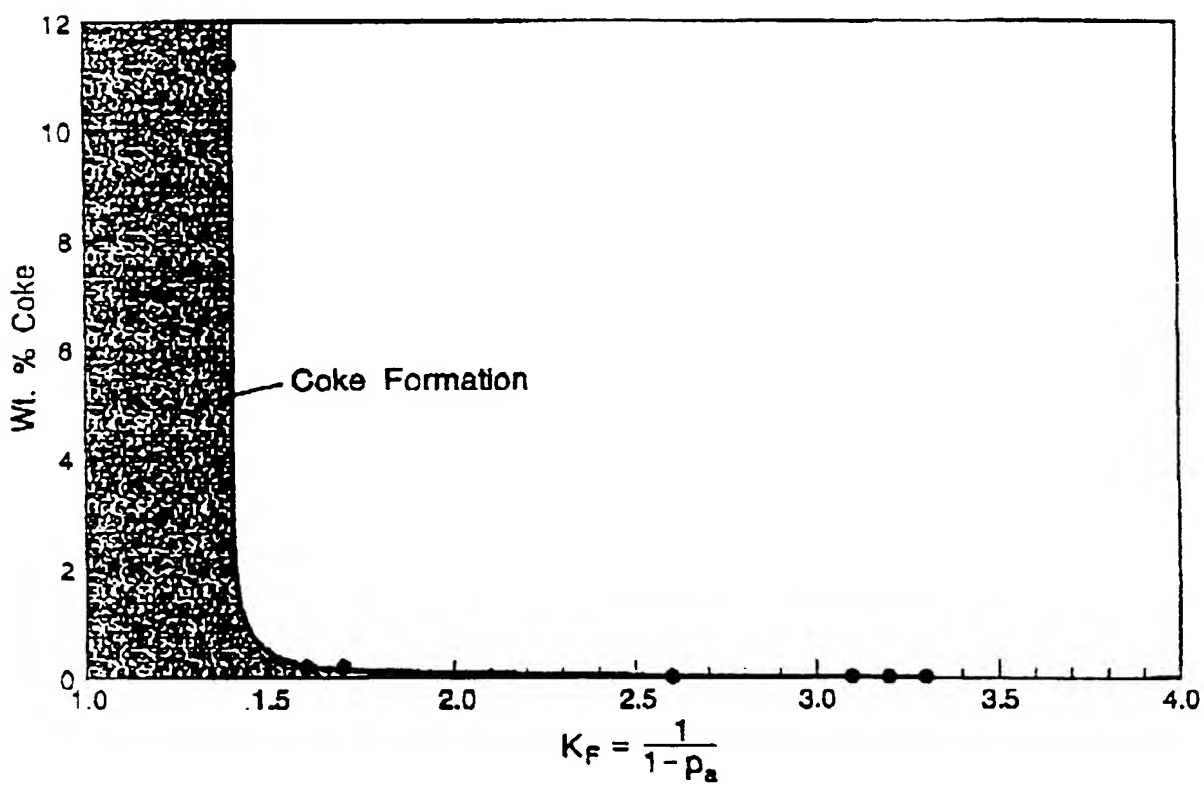


FIG. 11

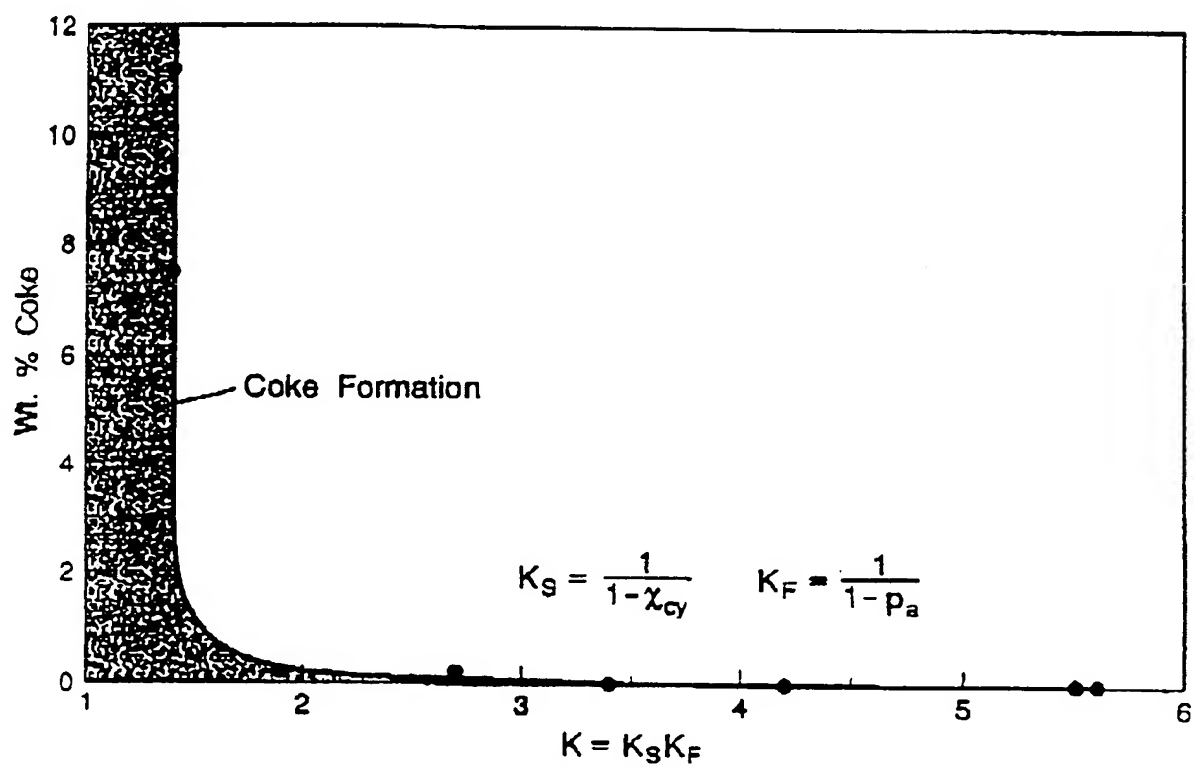


FIG. 12

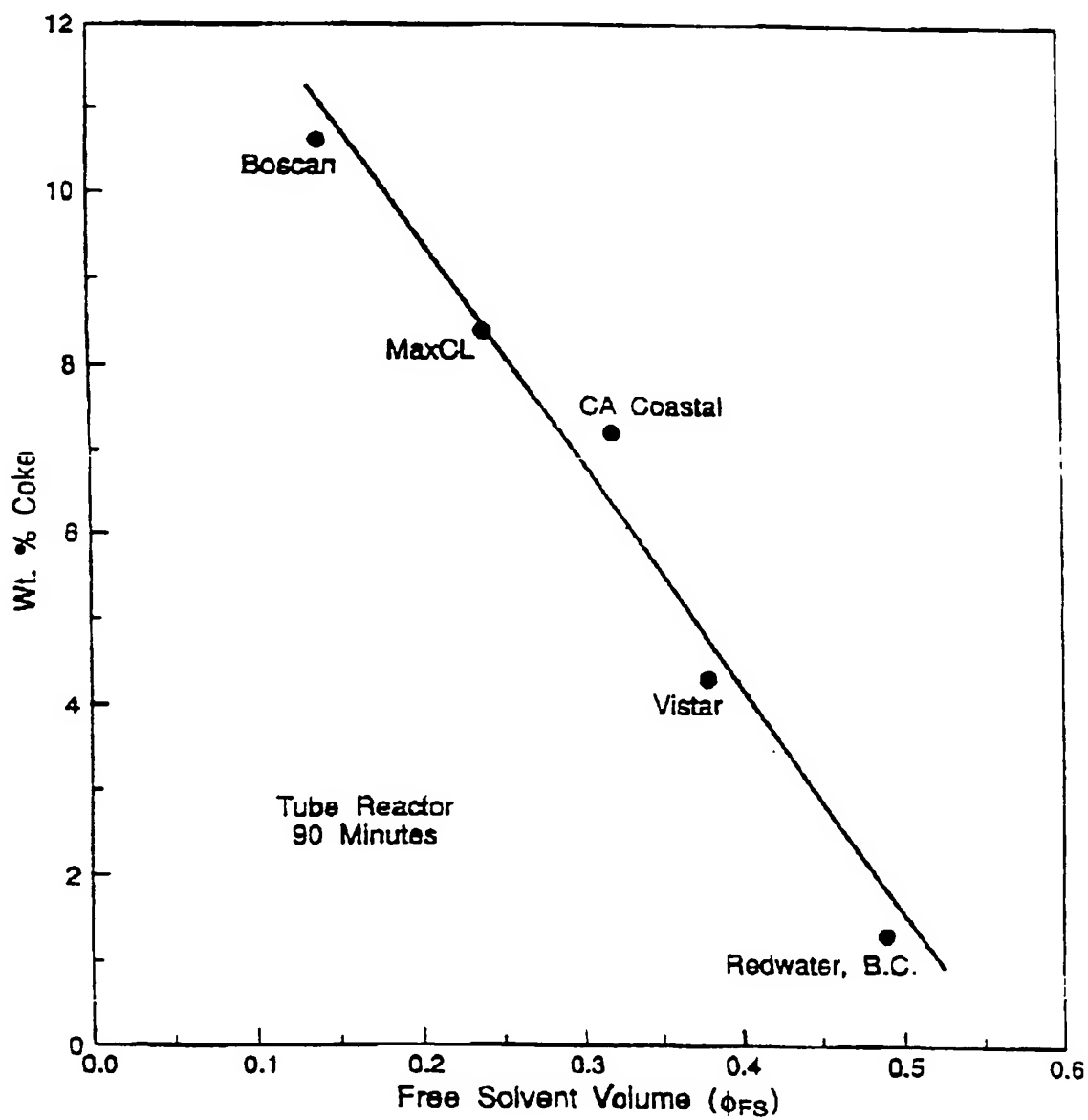


FIG. 13

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(81) Designated States (national): AE, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

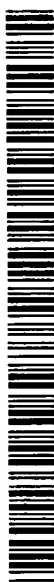
(88) Date of publication of the international search report:
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PREDICTING PROXIMITY TO COKE FORMATION

(57) Abstract: The invention may be used to evaluate suitability of hydrocarbon materials to various types of processing methodologies, or to determine processing parameters, either prior to processing or during processing. Prediction of proximity to formation of inhomogenous products may result in optimizing process parameters, or increasing output of desirable products, or decreasing energy use, or decreasing amounts of emissions of harmful compounds per unit of such hydrocarbon materials compared to conventional processing technology. Homogenous products produced with optimized conditions resulted from the application of the invention, may also have a higher level of purity.

WO 00/77120 A3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/15950

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : GO1N 35/08, 31/00, 31/16, 33/00

US CL : 436/55, 60, 139, 163

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 436/55, 60, 139, 163

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,628,204 A (MAES) 09 December 1986, col. 1, 2, 4	17-26, 30-36, 45-49, 63-71, 79-89, 92, 93
Y	US 4,493,765 A (LONG ET AL.) 15 January 1985, Abstract, col. 1, lines 18-30,	37, 38, 50-56
Y	US 5,574,215 A (BUNGER ET AL.) 12 November 1996, Abstract, col. 10, lines 43-55	57-62
Y	US 5,092,983 A (EPPIG ET AL.) 03 March 1992, Abstract, col. 3 (A), (B), col. 4 (C)	50-58
Y	US 5,861,228 A (DESCALES ET AL.) January 19, 1999, Abstract, col. 1, lines 60-68, col. 2, lines 1-10	54-56

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"O" document referring to an oral disclosure, use, exhibition or other means	

Document published after the international filing date or priority date claimed

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Date of the actual completion of the international search:

12 MARCH 2001

Date of mailing of the international search report:

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/15950

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PAULI ET AL. Book of Abstracts, 217th ACS National Meeting, Anaheim, CA, March 21-25 (1999), PETR-007. American Chemical Society: Washington, D.C.	57-62

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/15950

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 1-16
because they relate to subject matter not required to be searched by this Authority, namely:

Rule 67.1. No International Preliminary Examining Authority shall be required to carry out an international preliminary examination on an international application if, and to the extent to which, its subject matter is any of the following: (v) mere presentations of information
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims: it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/15950

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

- Group I, claim(s) 17-92, drawn to the method of processing a hydrocarbon material.
- Group II, claim 93, drawn to the apparatus for processing the hydrocarbon material.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: method and apparatus of Groups I and II share the same technical feature which is well known in the art, namely any device from the group of NMR spectrometer, NMR tomograph, mass spectrometer, IR spectrometer, Raman spectrometer, gel electrophoretic or size exclusion or paper chromatograph.

CORRECTED VERSION

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(43) International Publication Date
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(51) International Patent Classification⁷: G01N 35/08,
31/00, 31/16, 33/00

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(25) Filing Language: English

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(30) Priority Data:
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(71) Applicant (for all designated States except US): THE
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(74) Agent: MILES, Craig, R.; Santangelo Law Offices, P.C.,
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(US).

(81) Designated States (national): AE, AL, AM, AT, AT (util-
ity model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN,

CR, CU, CZ, CZ (utility model), DE, DE (utility model),
DK, DK (utility model), DM, EE, EE (utility model), ES,
FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID,
IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT,
LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL,
PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL,
TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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II

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ning of each regular issue of the PCT Gazette.

(54) Title: PREDICTING PROXIMITY TO COKE FORMATION

(57) Abstract: The invention may be used to evaluate suitability of hydrocarbon materials to various types of processing method-
ologies, or to determine processing parameters, either prior to processing or during processing. Prediction of proximity to formation
of inhomogenous products may result in optimizing process parameters, or increasing output of desirable products, or decreasing en-
ergy use, or decreasing amounts of emissions of harmful compounds per unit of sub hydrocarbon materials compared to conventional
processing technology. Homogenous products produced with optimized conditions resulted from the application of the invention,
may also have a higher level of purity

WO 00/77120 A3

PREDICTING PROXIMITY TO COKE FORMATION

I. TECHNICAL FIELD

Generally, methods and apparatus for evaluating or processing hydrocarbon materials having unimodal characteristics which may acquire multimodal characteristics upon processing. Specifically, indicators of stability for hydrocarbons having unimodal characteristics which may be used separately, or used in combination, or used in comparison to a determined threshold of instability for such unimodal characteristics, to assist in determining the proximity of hydrocarbon materials having unimodal characteristics to formation of multimodal characteristics, or to assist in pre-determining the degree of acquired multimodal characteristics in response to various processing parameters.

II. BACKGROUND

It can be difficult to evaluate, in response to a given set of processing parameters, if, or when, or to what degree, a hydrocarbon material of homogeneous mixture may transition to a hydrocarbon material of heterogeneous mixture to form carbon rich materials, such as coke. When hydrocarbon materials, such as heavy oils, petroleum residua, shale oils, coal tars, tar sand bitumen, asphalts, or the like, are processed at non-pyrolytic temperatures (at or below 340°C or 644 °F), or are heated above the temperature at which pyrolysis occurs (at about 340°C or 644 °F), there is typically an induction period before deposition of carbon rich materials occurs. This induction period can be variable, ranging from a few seconds to hours, depending on the particular hydrocarbon material and the temperature at which it is processed. To avoid deposition of carbon rich material, refiners often process hydrocarbon materials based on arbitrary criteria. Because arbitrary criteria are used, conventional processing of hydrocarbon materials can result in product yields that may not be maximal.

Because of the substantial benefits that can result from predicting if, when, or to what degree particular processing parameters may induce hydrocarbon materials to form heterogeneous mixtures, there has been extensive commercial interest in technology to determine indicators of stability, such as testing for the formation of coke, to predict thresholds of instability at which transition to the heterogeneous mixture may occur.

indicia of stability or thresholds of instability for hydrocarbon materials may be used, for example, to evaluate the suitability of hydrocarbon materials for particular types of processing, to predict the proximity to carbon deposition or coke formation, or for controlling hydrocarbon material processing in a manner which eliminates, minimizes, or predicts the amount of carbon deposition or coke formation. Even though commercial interest has generated substantial research in various fields, a long felt but unresolved need remains for methods of determining when hydrocarbon materials comprise homogeneous mixtures, or for development of indicia of stability for such homogeneous mixtures, or for more objective thresholds of instability for such homogeneous mixtures to assist in predicting proximity to formation of heterogeneous mixtures. See for example, United States Patent No. 5,853,565, hereby incorporated by reference. As such, substantial problems with respect to the evaluation of hydrocarbon materials for processing, or to the processing of hydrocarbon materials, remained unresolved.

A significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be the failure of conventional technology to define, provide measures for, or interpretations of, the dynamics of unimodal characteristics of intact hydrocarbon materials. Unimodal characteristics define a comprehensible pattern of attributes having predictable variation to changing environmental or processing parameters. As such, unimodal characteristics make possible the development of ascertainable indicia for comparative evaluation of the functionally related components that make up a hydrocarbon material. Ascertainable indicia can make the response of hydrocarbon materials to such environmental or processing parameters predictable. Unimodal characteristics may also provide objective indicia for the manufacture of hydrocarbon material products to assure that components have an anticipated degree of association. As can be understood, conventional technology has focused upon evaluation of the characteristics of separated components of hydrocarbon materials. The data obtained by evaluation of these isolated components is then typically used to determine the differences between types of hydrocarbon materials. However, conventional evaluation of isolated components does not provide a substantial amount of information about the intact hydrocarbon material itself. It can be understood that while conventional technology may understand that a hydrocarbon material is made up of chemical components, or that conventional technology may understand that

the chemical components have a certain physical relationship or distribution with respect to one another, conventional technology may provide, if at all, only a limited insight about the dynamic behavior of the various components of a hydrocarbon materials to changing environmental or processing parameters, or how the components functionally relate to maintain the stability of their physical association. As such, conventional technology may not provide suitable indicia of stability, thresholds of instability, or the methods for comparing such indicia of stability to such thresholds of instability which are the ascertainable measures of the unimodal characteristics of intact, unseparated hydrocarbon material. Indeed, conventional technology affords few, if any, tools for diagnosing or predicting how a hydrocarbon material will behave under a specific set of circumstances.

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be formation of carbon rich material during non-pyrolytic events (at or below about 340° C). The deposition of carbon rich material, such as coke, can result in fouling of heat exchange devices, or other refinery equipment in both upstream and downstream operations. This equipment may have to be shut down for mechanical coke removal as disclosed by Schabron, J. F. et al., Deposition From Heavy Oils, pp. viii and 2, (2000), hereby incorporated by reference.

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may also be the formation of carbon rich deposits, such as coke, from pyrolytic events (at or above about 340° C). Deposition of carbon rich material, such as coke, from pyrolytic events during processing can also result in the problems described above including having to shut down processing equipment for mechanical removal of the deposited materials.

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be the lack of a method or use of arbitrary criteria for predicting the proximity of a hydrocarbon material to the point of transition from a homogenous mixture of components to a heterogenous mixture of components, including the proximity to carbon deposition or coke formation.

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be the use of arbitrary criteria to assess the stability of a homogeneous mixture of hydrocarbon

materials, or to predict when carbon deposition may occur, can result in distillation parameters for the hydrocarbon material that stop the distillation sooner than need be to avoid deposition of carbon rich materials, such as coke. When distillation is stopped sooner than is necessary to avoid carbon deposition, it can result in less than maximal product yield from the hydrocarbon material. In 1997, for example, the average United States atmospheric and vacuum distillation refinery capacity was about 23 million barrels per day as disclosed by the Department of Energy, OIT Report, p. 5, (1998), hereby incorporated by reference. Solvent deasphalting capacity was about 0.3 million barrels per day. About 1.8 million barrels per day of heavy end feedstocks produced in 1997 from atmospheric and vacuum distillation columns and solvent-deasphalting units were input to thermal cracking and coking operations. This represents about 10% of the crude run. Id. at p. 49. An additional 6.5 million barrels per day went into catalytic cracking and hydrotreating units. Based on the total of 1.8 million barrels of total heavy ends minus about 0.3 million from solvent deasphalting, about 1.5 million barrels of heavy ends per day of thermal cracking and coking feed are produced from distillation operations. Assuming a one percent increase in United States distillate output because of efficiency improvements, an increase of about 15,000 average barrels per day of distillate and a corresponding reduction of heavy ends would result. Efficiency increases well above 1% could be possible if the proximity to carbon deposition or coking for a hydrocarbon material could be measured.

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be the inefficient use of energy. Coking operations use about 166,000-258,000 Btu per barrel of hydrocarbon material feed. Department of Energy, OIT Report, pp. 62-63, (1998). Hydrotreater energy use is comparable, and a similar consideration may apply. Since most of the energy used can be to initially heat all of the hydrocarbon feed material for distillation, there may be only minimal extra heat required to obtain a 1% improvement of distillate output at a particular temperature. For each 1% decrease in hydrocarbon material feed, there would be a potential savings of about 2.5-3.9 billion Btu with respect to hydrocarbon materials that do not need to be heated for coking, since they will have been recovered in an

another significant problem with conventional technology for the evaluation and

processing of hydrocarbon material may be high emissions. An energy savings of about 2.5-3.9 billion Btu per day, as discussed above, can result in a corresponding lowering of emissions from fuel that is not burned in processing operations. For example, residual fuel used as the heat source produces about 174 pounds of carbon dioxide per million Btu generated Department of Energy, OIT Report, pp. 27, (1998). Thus, in the U.S., the reduction in carbon dioxide emissions for each 1% industry-wide efficiency improvement may be about 218-679 tons per day!

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be financial losses. The disruption of hydrocarbon material processing from fouling due to deposition of carbon rich material, such as coke, is pervasive throughout the industry. The financial losses due to unscheduled downtime events as a result of non-pyrolytic, or of pyrolytic, deposition of carbon rich materials such as coke, may be difficult to quantify, but they are important.

Another significant problem with conventional technology for the evaluation and processing of hydrocarbon material may be that the liquid products of distillation may be of lower quality. Interrupting the distillation process, or proceeding with the distillation process in steps or stages, to avoid deposition of carbon rich materials or coke may allow for contamination of the liquid distillates.

Yet another significant problem with existing methods of processing hydrocarbon materials may be lack of a method for predicting the amount of initial deposition of carbon rich material or coke formation upon pyrolysis of a hydrocarbon material.

Still another significant problem with existing methods of processing of hydrocarbon materials may be the lack of apparatus or methods that are practical, convenient, or provide for real time data with respect to the stability of hydrocarbon materials.

With respect to processing hydrocarbon materials in general and specifically with respect to characterizing the dynamics of unseparated, intact hydrocarbon materials including predicting proximity to carbon deposition or coke formation, it can be understood there exists an array of problems which have remained unresolved by use of conventional hydrocarbon processing technology. The present invention addresses each

the above mentioned problems and provides a solution to each of them.

III. DISCLOSURE OF THE INVENTION

Indicia which define unimodal characteristics of hydrocarbon materials, or indicia which estimate the stability of such unimodal characteristics of hydrocarbon materials which may be used separately or may be used in combination, or may be used in

- 5 comparison to determined threshold of instability for such unimodal characteristics, to assist in determining the proximity of such unimodal characteristics to formation of multimodal characteristics, or to assist in predicting the degree of acquired multimodal characteristics in response to various processing parameters.

Naturally, as a result of these several different and potentially independent aspects of the
10 invention, the objects of the invention are quite varied.

A broad object of a particular embodiment of the invention can be to establish values for various associations between components of a hydrocarbon material which define the attributes or characteristics of a unimodal system. One aspect of this object can be to provide a value for the size of a core material in comparison to the size of the
15 core material having sufficient solvent solvation shell to maintain unimodal character (K_s). A second aspect of this object can be to provide an average value for the relative size ratio of a plurality of solvated core materials to the size of the plurality of solvated core materials having sufficient associated solvent (for example trapped solvent between them) to maintain unimodal character (K_F). A third aspect of this object can be to
20 provide a value for the solvation shell and associated solvent about a core particle or plurality of core particles to maintain unimodal characteristics (K) where $K = K_s \cdot K_F$.

A second broad object of a particular embodiment of the invention can be to provide indicia of stability for the above-mentioned unimodal characteristics exhibited by hydrocarbon materials. Indicia of stability are values that result from measuring the
25 degree of association between certain components in the hydrocarbon material which can allow assessment of the stability of a unimodal characteristic at a given point in time. Having objective values that reflect the instant degree of stability of the unimodal characteristics can be useful in evaluating suitability of hydrocarbon materials for various types of processing parameters, or for maintenance of unimodal characteristics during
30 hydrocarbon processing.

Another broad object of the invention can be to establish thresholds of instability. A threshold of instability establishes a degree of

association (or lack of association) between components of a hydrocarbon material at which acquisition of multimodal characteristics by the hydrocarbon material may be expected. These thresholds of instability may be used in conjunction with the above-mentioned indicia of stability to assess the proximity of hydrocarbon materials having unimodal characteristics to the threshold of instability or to acquisition of multimodal characteristics.

Another object of a particular embodiment of the invention can be to provide indicia of stability or to establish thresholds of instability based upon instrumented measurement of various size ratios which correlate with unimodal characteristics. The size ratio of the core material to the core material with associated solvent (K_s), or the size ratio of a plurality of solvated core materials in comparison to the size of the plurality solvated of core materials with associated solvent (such as trapped solvent between them) (K_F), or the solvation shell about a core particle or plurality of core particles (K) where $K = K_s \cdot K_F$, independently or in combination can be useful in measuring unimodal character of a hydrocarbon material. These size relationships may be evaluated by the use of various instrumented techniques such as nuclear magnetic resonance spectroscopy, nuclear magnetic resonance tomography, mass spectrometry, infrared spectrometry, raman spectroscopy, size exclusion chromatography, gel electrophoresis device, and paper chromatography.

Another object of a particular embodiment of the invention can be to provide indicia of stability related to the molecular weight of particular components in a hydrocarbon material which correlate with the stability of unimodal characteristics.

Another object of a particular embodiment of the invention can be to provide indicia of stability based upon the distribution of various polar components in hydrocarbon materials. One aspect of this embodiment of the invention may be an indicia of stability determined as the amount of asphaltenes soluble in particular solvent having a particular polarity. For example, the amount of asphaltenes precipitated with heptane soluble in cyclohexane can be diagnostic of the stability of the unimodal character of hydrocarbon materials. A second aspect of this embodiment of the invention can be an indicia of stability determined as the ratio of the weight percent of solvent soluble asphaltenes to the weight percent insoluble asphaltenes. For example, the ratio of the weight percent of the cyclohexane soluble portion of the

heptane precipitated asphaltenes to the weight per cent of the heptane precipitated asphaltenes appears to provide a sensitive indicator of stability of the unimodal character of hydrocarbon materials. A third aspect of this embodiment of the invention can be an indicia of stability based upon titration data. This involves the a titration of solutions of hydrocarbon material with a weak solvent to the point of asphaltene precipitation. An indicia of stability can be described based on the titration data defined as p_a/C_{min} .

Another object of a particular embodiment of the invention can be to use the determined indicia of stability in comparison to the established thresholds of instability to assess the proximity of unimodal characteristics to the threshold of instability. One aspect of this object of the invention can be to predict the proximity of a hydrocarbon material to coke formation.

Another object of a particular embodiment of the invention can be to use the indicia of stability, individually or in combination to evaluate hydrocarbon materials prior to processing or during processing to model substantially continuous distillation parameters for a particular hydrocarbon material or mixture hydrocarbon materials.

Another object of a particular embodiment of the invention can be optimization of the yields of distillable liquids from a hydrocarbon material having unimodal characteristics. Any increase in the yield of distillable liquids from the same amount of hydrocarbon material such as heavy oil or petroleum residuum provides an immediate increase in revenue. As such, a method of optimizing yields of distillable liquids has immediate and important commercial applications.

Another object of a particular embodiment of the invention can be to predict the degree of multimodal characteristics that may be acquired by a particular hydrocarbon material with respect to various processing parameters. One aspect of this object may be to predict the initial amount of carbon rich material, such as coke, that may be formed upon processing of a hydrocarbon material with particular processing parameters.

Another object of a particular embodiment of the invention can be to save energy. There may be a significant energy savings involved when a higher yield of distillates is produced from the same amount of hydrocarbon material. As described above, there may be only a minimal amount of extra heat required for a 1% improvement of distillate

yield. For example, if the yield of distillate is increased by 1%, the amount of heat required to process the hydrocarbon material for distillation is decreased by 1%.

distillate bottoms heated for a subsequent coking operation in the United States a potential savings in energy of about 2.5 billion Btu to about 3.9 billion Btu per day may be realized.

Another object of a particular embodiment of the invention can be to reduce
5 emissions. The above-mentioned potential savings in energy of about 2.5 billion Btu to about 3.9 billion Btu results in a corresponding reduction in emissions from fuel that is not burned in processing additional hydrocarbon material. For example, residual fuel used to as the heat source for processing produces about 174 pounds of carbon dioxide per million Btu generated. Department of Energy, OIT Report, p. 27 (1998), hereby
10 incorporated by reference. Thus in the United States, the reduction in carbon dioxide emission for each 1% industry-wide efficiency improvement is about 218-679 tons.

Another object of a particular embodiment of the invention can be to produce higher initial quality as compared to conventional liquid distillables. Because the process of distillation may be nearly continuous, the distillates may have fewer
15 opportunities to collect water and become otherwise contaminated. This may result in higher purity distillates and perhaps lower post distillation processing costs. As such, distillates from near continuous distillation processes made possible from the instant invention may be distinguishable from conventional distillation products.

Still another object of a particular embodiment of the invention can be to provide
20 a molecular weight/polarity map system to assess the solubility of various components in a mixture of asphaltene complexes at various distillation parameters. Such a map system may provide an evaluation method for diagnosing processing conditions for hydrocarbon materials having unimodal characteristics prior to or during distillation.

Yet another object of a particular embodiment of the invention can be to establish
25 a sequential solvent extraction system to isolate various asphaltene complexes from hydrocarbon materials having unimodal characteristics based on molecular weight or polarity.

Naturally further objects of the invention may be disclosed throughout other areas of the specification and claims.

FIGURE 1

Figure 1 shows the relationship between solubility and solubility parameter

difference.

Figure 2 shows the effects of molecular weight and solubility parameter difference on solubility.

Figure 3 shows a flow diagram of the hydrocarbon material solvent extraction sequence and solubility parameters of solvents.

Figure 4 shows a molecular weight polarity map.

Figure 5 shows elution profiles of high performance size exclusion chromatography of various amounts of material A from fraction 4.

Figure 6 shows elution profiles of high performance size exclusion chromatography of maltenes.

Figure 7 shows titration results for three stripper bottoms.

Figure 8 shows weight percent coke relative to values for the indicia of stability_{pa/Cmin}.

Figure 9 shows weight percent coke relative to values for the indicia of stability_{y x} based upon the weight percent of precipitated asphaltenes soluble in a second solvent over the weight percent of precipitated asphaltenes.

Figure 10 shows weight percent coke relative to values for the indicia of stability_{Ks}.

Figure 11 shows weight percent coke relative to values for the indicia of stability_{KF}.

Figure 12 shows weight percent coke relative to values for the indicia of stability_K.

Figure 13 shows a graph of weight percent coke relative to values for the indicia of stability_{φFS}.

V. MODE(S) FOR CARRYING OUT THE INVENTION

Hydrocarbon materials, such as heavy oils, petroleum residua, coal tars, shale oils, asphalts, or the like can comprise polar core materials, such as asphaltenes, dispersed in lower polarity solvent(s). Intermediate polarity material(s), usually referred to as resin(s), can associate with the polar core materials to maintain a homogeneous mixture of the components. The invention focuses on novel unimodal characteristics of these components that can maintain the hydrocarbon material as a homogeneous mixture.

Alternately, the lack of, or diminishment of these ascertainable aspects of the unimodal character can be used to predict the onset or degree of acquired (and perhaps undesirable) multimodal characteristics associated with formation of the resulting heterogeneous mixture.

5 As one example, refinery processes, including but not limited to, atmospheric or vacuum distillation, visbreaking, hydrocracking, delayed coking, Fluid Coking, FLEXICOKING, or Eureka that convert hydrocarbon materials to lighter distillate fuels require heating for distillation, hydrogen addition, or carbon rejection (coking). However, when using conventional refinery processes, the efficiency of converting such hydrocarbon material may be limited by transition of the hydrocarbon material of
10 homogeneous mixture to a hydrocarbon material of heterogeneous mixture. The transition to the heterogeneous mixture may include the formation of insoluble carbon-rich coke deposits, including the formation of coke. As such, any reduction in carbon deposition, or increase in the distillation yield during the thermal processing of hydrocarbon material
15 can have a significant impact on the manner or economics of hydrocarbon processing.

The invention, in contrast to conventional processing technology, provides ascertainable unimodal characteristics as the basis for measures of stability with respect to hydrocarbon materials that transit between homogeneous mixtures and heterogeneous mixtures of components, methods for assessing the degree of the such unimodal
20 characteristics, methods for predicting the proximity of hydrocarbon materials having unimodal characteristics from the threshold of acquiring multimodal characteristics, or methods for predicting the degree of multimodal characteristics acquired due to various processing parameters.

Specifically, the invention provides indicia of stability, thresholds of instability,
25 methods for comparing such indicia of stability with such thresholds of instability so that hydrocarbon materials can be evaluated for processing, for selecting processing parameters to avoid carbon deposition, or for reaching predetermined levels of carbon deposition, for increasing the yield of liquid distillates, for decreasing emissions from processing, or for reducing the consumption of energy. In this application, each are
30 disclosed as part of the results shown to be achieved by the various methods and devices

As the various methods and devices are disclosed, it should be understood that these are accomplished using certain

devices but also that the methods and devices can varied in a number of ways. Importantly, as to all of the foregoing, all of these facets should be understood to be encompassed by this disclosure.

The dissolution of a material in a solvent, or the mixing of two liquids to form a homogeneous mixture, will occur if the free energy of the process is zero or negative as described by:

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the free energy, ΔH is the heat of mixing, T is the temperature, and ΔS is the change in entropy. Typically in a dissolution process, the entropy term is relatively large, and the heat of mixing determines if the mixing will occur.

The heat of mixing may be described as:

$$\Delta H = V ((\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2})^2 \Phi_1 \Phi_2$$

where ΔH is the heat of mixing, V is total volume, ΔE_x is the molar energy of vaporization of component x , V_x is the molar volume of component x , and Φ_x is the volume fraction of component x in the solution. The term $(\Delta E/V)^{1/2}$ is called the solubility parameter δ and is typically given in units of $(\text{cal/cc})^{1/2}$, called the Hildebrand. Numerical values for the solubility parameter of a solvent can be calculated as:

$$\delta = (\Delta E/V)^{1/2}$$

from the molar energy of vaporization to the ideal gas state, ΔE and the molar volume V . For large molecules or polymeric systems, group contributions can be used to calculate if the density of the material is known or can be estimated.

The heat of mixing two materials is dependent on the difference between their solubility parameters squared, $(\delta_1 - \delta_2)^2$. If the solubility parameters are identical, the heat of mixing is zero and the dissolution/mixing process is driven by the entropy term $T\Delta S$ alone, and mixing will occur. If the solubility parameters are not identical, the term $(\delta_1 - \delta_2)^2$ will have a net positive value, which will cause the energy term ΔH to oppose mixing. If the energy term ΔH is greater than the entropy term $T\Delta S$, mixing will not occur.

However, the use of the solubility parameter is complicated by the presence of dipole and hydrogen bonding interactions. For solvents or materials with strong polarity or hydrogen bonding components, dissolution may not be predictable by the single component, or dispersion solubility parameter, described above. For such systems, solubility is maximized when all the components for the solvent and material being dissolved are similar in polarity. Two- or three-dimensional maps can be used to describe so-called solubility zones, areas, or spheres for such systems. Mixtures of solvents with different solubility parameter components can be used to generate a mixture with custom-formulated solubility parameter components. Thus, it is possible to formulate a mixture of two or more solvents that will dissolve a material that is not soluble in one or more of the solvents alone. For hydrocarbon materials such as petroleum residua or fractions isolated therefrom, solubility characteristics can best be described by the single-component dispersion solubility parameter. Multi-component solubility parameters are not necessary.

Selected solvents that do not have significant polarity or hydrogen bonding components are listed in Table 1, along with their solubility parameters. The solubility parameter of a mixture of solvents is the sum of the solubility parameter of each component times the volume fraction of that component in the mixture.

Table 1. Solubility Parameters of Solvents with Predominantly Dispersive Components

	Solvent	Solubility Parameter, $(\text{cal/cc})^{1/2}$
5	perfluoro-n-hexane	5.9
	iso-octane	6.9
	n-pentane	7.0
	n-hexane	7.3
	n-heptane	7.4
10	cyclohexane	8.2
	toluene	8.9
	benzene	9.2
	carbon disulfide	10.0
	diiodomethane	11.8
15		

Toluene, for example, is known to be a good solvent for hydrocarbon material such as whole petroleum residua. This is probably because the solubility parameters of whole petroleum residua components lie within about $\pm 2 (\text{cal/cc})^{1/2}$ of 8.9, or within 6.9 - 10.9 $(\text{cal/cc})^{1/2}$. Once thermal treatment of petroleum residua has begun, however, toluene fails to solvate the more polar components, which are formed as carbon deposition or coking ensues.

Relatively large solubility parameters require the use of polar interactive or hydrogen bonding solvents such as the alcohols (methanol $\delta = 14.6$, ethanol $\delta = 12.5$, etc.). Solubility parameters below those of the perfluorinated hydrocarbons can be attained by using silicone oils or supercritical fluids such as supercritical carbon dioxide.

Hydrocarbon materials, such as petroleum residua, are usually complex mixtures that are usually separated into well-defined fractions prior to characterization. Separation schemes typically include steps such as precipitation of asphaltenes by a hydrocarbon solvent, precipitation of maltenes and asphaltenes by a non-solvent, precipitation of asphaltenes (maltenes) by adsorption, ion exchange, size exclusion chromatography, or combination

thereof as disclosed by Schabron, J.F., G.W. Gardner, J.K. Hart, N.D. Niss, G. Miyake, and D.A. Netzel, The Characterization of Petroleum Residua, United States Department of Energy Report DE/MC/11076-3539 (1993), hereby incorporated by reference. The isolation of components from hydrocarbon materials, such as asphaltenes, can be based upon a solvent separation procedure based on the solubility difference between the precipitating solvent and the precipitated material. The solubility (or lack thereof) of components of hydrocarbon materials can be dependent on both molecular weight and polarity considerations. The solubility parameter of a particular hydrocarbon material or residuum fraction probably constitutes a range that is reflective of the variety of chemical components of the fraction. The solubility parameter difference that results in a phase separation of two materials, such as asphaltenes in a solvent can be estimated using the Scatchard-Hildebrand equation, which involves several assumptions that take into account both the heat of mixing and entropy terms:

$$\ln a_a = \ln x_a + M_a/RT\rho_a \cdot [N_s^2(\delta_s - \delta_a)^2]$$

where a_a is the activity of the solute a, x_a is the mole fraction solubility of a, M_a is the molecular weight of a, ρ_a is the density of a, N_s is the volume fraction of solvent, and $(\delta_s - \delta_a)$ is the difference between the solubility parameters of the solute a and the solvent s. Assuming that the activity of asphaltenes a_a is 1 (solid asphaltenes in equilibrium with dissolved asphaltenes as an example) and the volume fraction of an excess of solvent is essentially 1, the equation can be rearranged into a form that can be used to gain insight into the solubility of asphaltenes:

$$\ln x_a = -M_a/RT\rho_a \cdot [(\delta_s - \delta_a)^2]$$

Assuming molecular weights of 750 and 1,500 g/mole for two hypothetical asphaltene molecules, the solubility as a function of the differences between solubility parameters of the asphaltene molecules and a range of solvent solubility parameters can be calculated.

individual asphaltene molecule or complex decreases as the difference between solubility

parameters increases. Also, a lower molecular weight molecule is more soluble than the higher molecular weight molecule for a particular difference in solubility parameter.

From the above equations, it is apparent that the solubility depends both on molecular weight and polarity of the particular asphaltene molecule or associated specie. In an asphaltene mixture, for example, there exists a polarity and molecular weight continuum as described by Schabron, J.F. and J.G. Speight, *The Solubility and Three-Dimensional Structure of Asphaltenes*, Petroleum Science and Technology, 16 (3-4), pp. 361-376 (1998), hereby incorporated by reference.

Now referring to Figure 2, additional information can be gleaned by calculating the solubility parameter difference at several molecular weights ranging from 100 - 10,000 g/mole at which the solubility of asphaltenic or other material is a mole fraction of about 0.001 (0.1 %, or 1,000 ppm). The results of this calculation defines a phase diagram that is a function of molecular weight and solubility parameter difference. As can be understood from the figure both polarity and molecular weight of asphaltenes in a solvent define the solubility boundary. This conceptually describes how asphaltenes can be precipitated from hydrocarbon materials, which can be considered a type of homogeneous mixture having a continuum of molecular weights and polarities which exhibit or have certain unimodal characteristics. Figure 2 also shows in a generalized manner that as the molecular weight of a particular solute decreases, there is an increased tolerance to polarity difference between solute and solvent under miscible conditions.

The absolute difference in solubility parameters that will result in transition from the homogeneous mixture exhibiting unimodal characteristics to the heterogeneous mixture exhibiting or having multimodal characteristics such as a two-phase system (or other poly-phase system), or precipitation of a component, or deposition of carbon, for a particular system is not straightforward. Based on the above discussions and the results illustrated in Figure 2, some generalizations can be made. For a polymer to dissolve in a solvent, the solubility parameter of the solvent should be within about 1 (cal/cc)^{1/2} of the solubility parameter of the polymer. For a non-polymeric solid material, such as naphthalene, to dissolve in a solvent, the difference in solubility parameters should be less than about 2 (cal/cc)^{1/2}. And finally, for two liquids to be miscible, the difference in

solubility parameters should be less than about 1 (cal/cc)^{1/2}.

Now referring to Figures 3 and 4, and the above discussion, an embodiment of

the invention can be a molecular weight - polarity map developed specifically for hydrocarbon material components. A molecular weight - polarity map can have a first axis having values relating to molecular weight. It may also have a second axis having values relating to solubility parameter. As can be understood, a particular molecule or associated specie in a hydrocarbon material occupies a single point, or molecular weight - polarity coordinate location (3) on, on the map. A mixture of molecules or mixture of molecules with associated species forming a continuum of polarity or apparent molecular weight values or a combination of both (either of individual molecules or individual molecules with associated species) can be visualized as occupying a particular area on the map. For a particular solvent, the solubility of a solute increases with decreasing polarity, decreasing apparent molecular weight, or a combination of the two. As a hydrocarbon material undergoes thermal alteration, solvent perturbation, or aging, the changes in the molecules or associated species can cause the points representing these materials to move to a different region of the map. This movement can illustrate at least one unimodal characteristic of hydrocarbon materials. Interestingly, the core material can comprise a variably adjustable core material having a molecular weight responsive to temperature change. Also, it is important to note that the core material may have polarity which is stabilized within a region of solubility even when the molecular weight may change. Thus, such a map can be used as a means of evaluating the characteristics of hydrocarbon materials or diagnosing processing conditions or the state of thermal degradation. It can also be used as a tool in efforts to diagnose and possibly intervene in the incipient precipitation of polar materials during hydrocarbon material processing.

One embodiment of the phase diagram map can be developed by calculating the core material solubility regions, including the solubility region of asphaltenes, by determining solubility of core materials or asphaltenes in a variety of solvents. For example, solvents ranging from iso-octane, with a solubility parameter of $6.9 \text{ (cal/cc)}^{1/2}$, to carbon disulfide, with a solubility parameter of about $10.0 \text{ (cal/cc)}^{1/2}$. As shown by Figure 4, the core material solubility region (1) can comprise between about $6.9 \text{ (cal/cc)}^{1/2}$ to about $11.0 \text{ (cal/cc)}^{1/2}$. The map can be based on solubility-parameter-tuned solvent mixtures providing even spacing between a plurality of solvent tuned contour

lines. For example, the map can be based on solvent mixtures of iso-octane (I) and CS₂ where the spacing can be 0.5 $\text{(cal/cc)}^{1/2}$. The border between the

soluble and insoluble regions is defined arbitrarily as the solubility of a mole fraction of 0.001 (0.1 %, or 1,000 ppm). This border is actually a point on a solubility gradient, where solubility increases towards the left-hand portion of a curve and decreases to the right. Naturally, other solvents or combinations of solvents could be used to create a range of solubility parameters having a different number or spacing with respect to the solvent tuned contour lines. As shown by Figure 4, a particular embodiment of the molecular weight -polarity map can be established by using a first solvent tuned contour line based on iso-octane, a second solvent contour line based on heptane, a third solvent tuned contour line based on heptane:toluene (2:1)(v:v), a fourth solvent tuned contour line based on heptane:toluene (1:2)(v:v), a fifth solvent tuned contour line based on toluene, a sixth solvent tuned contour line based on toluene:carbon disulfide (55:45) (v:v), and an eighth solvent tuned contour line based on carbon disulfide.

The molecular weight - polarity related coordinate location (3)(for clarity not all the coordinate locations have leaders and identification numbers) of a particular material on the map was determined by three measurements. First, a solubility or solvent spectrum of the material was obtained to determine between what lines on the map the material lies. This was accomplished by performing a series of solubility measurements in a series of solvents of increasing or decreasing solubility parameters and determining their weight percentages of the soluble material. Excess solvent to solute (40:1 v:w) ratios were used to minimize any potential effect of the solute on the overall solubility parameter of the system. Second, a number average molecular weight of the molecules or associated species mixture was determined on the isolated fractions using vapor pressure osmometry in toluene at 60° C. Third, the isolated fractions were analyzed using analytical-scale size exclusion chromatography.

Ideal materials for demonstrating how the molecular weight- polarity map invention may apply to thermally treated hydrocarbon material having unimodal characteristics are bench-scale stripper bottoms oils (although the example is not meant to reduce the scope of invention to such materials or to such scale) which were generated as listed below:

A. Stripper Bottoms – 273 °C (525 °F)

C. Stripper Bottoms – 273 °C (525 °F)

These three stripper bottom represent a series of increasing severity of thermal treatment at atmospheric pressure for the same hydrocarbon material. In the sequence of increasingly severe treatment, the A bottoms were fed into the B unit, whose bottoms were fed into the C unit. These particular materials were allowed to remain in the
5 strippers as they cooled down. Both Materials A and B were fully soluble in toluene, while Material C contained 13.5 weight percent toluene insoluble material, which yielded 17.9 weight percent ash.

With respect to the first measurement, as discussed above and now referring to Figure 3, a solubility or solvent spectrum of the material was obtained using the solvent
10 extraction sequence illustrated. All solvents used were reagent grade or better from commercially available sources. Iso-octane asphaltenes were first obtained by heating the whole residua with a 40:1 (v:w) portion of iso-octane to about 70 °C for 1 hour with stirring. The mixture was stirred at room temperature overnight, then allowed to set for at least 0.5 hour prior to vacuum filtering through a medium frit (10-15 µm) sintered
15 glass filter. To remove solvent from the insolubles, air was passed through the filter for 5 min, they were placed in a vacuum oven at 120 °C and 23 inches Hg vacuum for 1 hour, were cooled, then weighed. A 40:1 ratio (v:w) of n-heptane was mixed with the insolubles and stirred overnight. The insolubles were filtered using vacuum filtration through a medium glass filter. These steps were repeated with the series of solvents
20 shown in Figure 4. At the end of the series, the carbon disulfide insolubles (including coke) were ashed in a muffle furnace at 400 °C overnight to obtain weight percent ash.

With respect to the second measurement, number average molecular weights were determined with a Knauer vapor pressure osmometry (VPO) instrument using toluene at 60°C (ASTM D-2503). Determinations were made with 1- 4 weight percent
25 sample solutions. Benzil was used for calibration.

With respect to the third measurement, high-performance analytical scale size exclusion chromatography (SEC) results for the fractions are listed in Table 3. Portions of 150 µL of 0.2 weight percent solutions of the fractions were injected (0.3 mg). The values are reported relative to polystyrene standards having known molecular weight
30 analyzed under the same conditions. As such, the standards must be used with caution since polystyrene and the hydrocarbon materials are not the same type of materials.

The compiled data for the three stripper bottoms materials are presented in Table 2. Again referring to Figure 4, the molecular weight - polarity map invention developed from the data and the effects of the thermal treatment on the three heavy oils prior to and during coke formation. The molecular weight - polarity map invention "peels" the layers of association with respect to a hydrocarbon material having unimodal characteristics. The gravimetric data show the progression towards more polar species as the severity of thermal treatment increases. Material C is generating both carbon or coke, or carbon or coke precursors (Fractions 6 and 7).

Table 2. Solubility Map Data for Three Stripper Bottoms

10

Sample Measurement			Fraction (See Figure 3.)							coke	ash
			1	2	3	4	5	6	7		
15	A	Weight Percent	85.9	0.8	6.3	5.1	0.7	1.1	0.1	<0.1	<0.1
		VPO Mn g/mole	474	1260	4040	17000	23000	-	-	-	-
		δ (cal/cc) ^{1/2}	8.4	9.2	8.8	8.8	9.2	-	-	-	-
	B	Weight Percent	83.4	0.9	6.7	5.5	1.0	2.2	0.1	0.2	<0.1
		VPO Mn g/mole	542	1180	3580	12000	14000	-	-	-	-
		δ (cal/cc) ^{1/2}	8.4	9.2	8.8	8.8	9.2	-	-	-	-
20	C	Weight Percent	64.0	2.0	5.3	5.8	2.9	4.5	1.5	11.5	2.5
		VPO Mn g/mole	516	684	1320	2920	6800	-	-	-	-
		δ (cal/cc) ^{1/2}	9.0	9.9	9.6	9.5	9.5	-	-	-	-

The data also show that the number average molecular weights of the iso-octane-soluble maltenes are about the same for all three oils. The molecular weight of each of the more polar fractions decreases significantly with thermal treatment. The main difference between the various polar fractions for a particular material seems to be molecular weight. The solubility parameters are similar for a particular series of polar materials with large differences in apparent molecular weight. This leads to the speculation that a residua colloidal system self-adjusts to lower the overall energy of the system by matching as closely as possible the polarity of the associated complexes to the solvent matrix (iso-octane maltenes). This appears to occur automatically regardless of the apparent molecular weights of the complexes.

For the pyrolysis series, the higher molecular weights are probably due to associated species, which the thermal treatment is breaking apart. This results in an overall less stable colloidal-type system with increasing severity of thermal treatment, as was observed with the Heithaus titration data discussed below. Also, significant cracking has taken place in Material C, which further reduces the apparent molecular weight of the corresponding fractions soluble in the various solvents compared to Materials A and B. The solubility parameters (polarities) of the fractions from C are larger than the corresponding fractions from A and B. The data clearly show some significant differences between Material C, and the less severely treated Materials A and B.

10

Table 2. High-Performance Size Exclusion Chromatography Results

	Fraction	Size Exclusion Chromatography			VPO	
		Mw	Mn	Range ^a	Mw/Mn	Mn
15	A (273 °C/525 °E)					
	1	928	422	210-2200	2.20	474
	2	1490	585	270-3400	2.55	1260
	3	2440	772	340-5600	3.16	4040
	4	2240	618	260-5400	3.62	17000
20	5	2120	523	210-5300	4.05	23000
	B (343 °C/650 °F)					
	1	923	439	220-2100	2.10	542
	2	1320	539	250-3000	2.45	1180
	3	2110	703	310-5000	3.00	3580
25	4	2090	611	260-5000	3.42	12000
	5	1930	510	210-4800	3.78	14000
	C (371 °C/700 °F)					
	1	705	395	210-1500	1.78	516
	2	788	388	190-1800	2.03	684
30	3	1140	481	220-2600	2.37	1320

- a. From elution volumes at 10% to 90% of peak area

Except for the number average molecular weight values for the extracted iso-octane maltenes for all three materials (Fraction 1), the values are significantly lower than the number average molecular weight values determined by VPO. The discrepancy cannot be wholly attributed to the use of polystyrene standards and the non-uniform response with refractive index detection from residual components of differing functionality. Some adsorption of materials on the polystyrene-divinylbenzene stationary phase may be occurring also. The values determined by VPO represent the apparent number average molecular weights in 1 - 4 weight percent toluene solutions. An additional possible effect may be that associative complexes that give apparent high VPO molecular weight values in solution break down during the SEC separation for Fractions 4-5 for all three materials, resulting in significantly lower apparent number average molecular weight values than the corresponding VPO values. To check this further, various amounts of one of the fractions for which sufficient material was available were injected onto the high-performance SEC column. The fraction was Material A, Fraction 4 which gave an apparent VPO molecular weight of 17,000 g/mole and a SEC number average molecular weight of 618 g/mole (Table 2).

Now referring to Figure 5, which shows the results from injections of 100 μ L of toluene solutions containing 0.3 - 15 mg onto the SEC column. As more material was injected, the retention volume decreased, indicating an increase in associations or apparent molecular weight. For the 7.5 mg injected, the peak split into two peaks, suggesting the presence of significant associations. This peak splitting and elution volume shortening phenomenon was not observed when a polystyrene standard with a molecular weight of 400 g/mole was injected under identical conditions. Thus, the peak splitting phenomenon is not likely due to overloading the column with sample. For injections of 0.3 to 7.5 mg, the material eluted in about 3 mL of toluene. The concentration at which significant complex formation begins for this asphaltenic material is estimated to be at the point where the peak splits. This occurs somewhere between 1.5 and 3.0 mg. The injected diluted sample concentration is estimated to be between about 0.00 - 0.5 weight percent. This result may be consistent with the results of

Andersen and Birdie, who reported a critical micelle concentration of asphaltenes in toluene near 0.38 weight percent using calorimetric titration. Andersen, S.I. and K.S. Birdi, Aggregation of Asphaltenes as Determined by Calorimetry, Journal of Colloid and Interface Science, 142, pp. 497-502 (1991).

5 As can be understood from the table, as with the VPO data, the SEC number average molecular weights for a particular fraction generally decrease with increasing severity of thermal treatment. The polydispersity M_w/M_n , an indicator of molecular weight distribution, also decreases for a particular fraction with increasing severity of thermal treatment.

10 Now referring to Figure 6, chromatograms appeared as essentially symmetrical peaks with one exception — the iso-octane maltenes (Fraction 1). These chromatograms show a leading high molecular weight shoulder component (4) in the 273 °C (525 °F) material, which was smaller for the 343 °C (650 °F) material and was not evident for the 371 °C (700 °F) material. As such, this component of the iso-octane maltenes having an
15 apparent high molecular weight appears to be related to at least one unimodal characteristic of hydrocarbon materials which can be destroyed with increasing severity of thermal treatment.

An embodiment of the invention based on this finding comprises an indicia of stability_{usc} based upon the steps of detecting this unimodal characteristic stability
20 component having apparent high molecular weight. This approach may comprise providing a hydrocarbon material component analysis device, or devices in combination, which can be a size exclusion chromatography device as described above, or could also be other devices for identifying the apparent high molecular weight unimodal stability component such as a mass spectrometry device, an infrared spectrometry device, a raman
25 spectroscopy device, gel phoresis device, paper chromatography device, or nuclear magnetic resonance device. Naturally, each hydrocarbon analysis device could be configured, as would be well known to those of skill in the art, so that the unimodal characteristic stability component could be identified. While in the example above, maltenes were extracted into iso-octane, other solvents, or other devices could be used to
30 isolate the corresponding maltenes containing the unimodal characteristic stability

component. The step of identifying the unimodal characteristic stability component could comprise observing elution of the apparent molecular weight

of the unimodal characteristic stability component directly as described above for size exclusion chromatography where the apparent molecular weight can be equal to or larger than about 500 gram per mole. As the amount of the unimodal characteristic stability component approaches zero continued thermal processing results in carbon deposition including coke formation.

Now referring to Figure 7, in addition to the above-mentioned three measurements, automated Heithaus titration was performed with the toluene-soluble components of hydrocarbon material (although other dissolvents could be used such as benzene, xylene, ethylbenzene, similar aromatic hydrocarbons). This method comprises preparing three toluene solutions at different concentrations of hydrocarbon material. Each can be titrated with a weak solvent such as iso-octane (although other weak solvents could be used such as pentane, hexane, heptane, hexadecane, or similar aliphatic hydrocarbons) with a titration device. The weight of residua or asphalt (W_a), the volume of toluene (V_s), and volume of iso-octane titrant (V_t) are recorded at the flocculation point where asphaltenes just begin to precipitate for each solution. The flocculation ratio and dilution concentration are calculated as follows:

$$FR = \text{Flocculation Ratio} = V_s / (V_s + V_t)$$

$$C = \text{Dilution Concentration} = W_a / (V_s + V_t)$$

A plot of FR versus C can be made and the intercepts determined (FR_{\max} and C_{\min}). The Heithaus parameters are defined as follows:

$p_a = 1 - FR_{\max}$	Peptizability of Asphaltenes
$p_o = FR_{\max} \times (1/C_{\min} + 1)$	Solvent Power of Maltenes
$P = p_o / (1 - p_a) = 1/C_{\min} - 1$	Overall Compatibility of Residua

Larger values of p_a may indicate more peptizable asphaltenes, and larger values of P indicate an overall compatible system. A larger p_o value is subject to a mixed interpretation.

The Heithaus parameters for the three bottoms materials are shown in Table 4. The results show that the three bottoms materials are becoming less stable with

increasing severity of thermal treatment. The results also show a significant difference between Material C, which is producing coke or carbonaceous material, and Materials A and B, which are not yet near coke production or carbon deposition.

Table 4. Heithaus Titration Results for Three Stripper Bottoms

Heithaus Parameter	Material		
	A (525 °F)	B (650 °F)	C (700 °F)
p_a	0.668	0.638	0.364
p_o	0.766	0.805	1.09
P	2.31	2.23	1.71
p_a/C_{min} Ratio	0.87	0.78	0.26

Another way of evaluating FR_{max} can be that it is the volume fraction of toluene in a toluene- iso-octane mixture, assuming additive volumes. By knowing the solubility parameter of both solvents, the solubility parameter at FR_{max} can be calculated. FR_{max} is thus a measure of the solubility parameter at infinite dilution at which asphaltenes begin to precipitate. Such measurements also may have applicability in predicting precipitation of asphaltenes for mixtures of two or more residua. A relatively larger FR_{max} indicates a less soluble asphaltene. Since solubility depends on both molecular weight and polarity, this can be due to a higher molecular weight or more polar asphaltene, or both. C_{min} is the ratio of residua to titrant (iso-octane for this example although other solvents can be used) at which asphaltenes begin to precipitate. A larger C_{min} indicates a less compatible system (smaller P). Assuming that asphaltene flocculation occurs at a particular solubility parameter for a particular residua, it is apparent that both FR_{max} and C_{min} and the line connecting them are at the same solubility parameter.

The solubility parameter at which asphaltenes begin to precipitate (at FR_{max}) and the solubility parameters of the residua matrix (at C_{min}) were calculated and are listed in Table 4. The three stripper bottoms A, B, and C are shown in Figure 1. As the severity of thermal treatment increases, the solubility parameter of the onset of asphaltene flocculation increase with

increasing severity of thermal treatment. The material that has been heated to the point of coke production is significantly more polar than the same material prior to coke production. This is also reflective of cracking and the removal of less polar distillates with heating.

5 Table 5. Solubility Parameters for Whole Residua and Asphaltene Precipitation Onset

Solubility Parameter, δ (cal/cc) ^{1/2}			
Material	Whole Residua	Asphaltene Precipitation Onset	
10	A (525 °F)	8.4	7.6
	B (650 °F)	8.5	7.6
	C (700 °F)	9.1	8.2

Now referring to Table 4, another embodiment of the invention based on the titration data provides an indicia of stability defined as p_a/C_{min} . This indicia of stability p_a/C_{min} can be based on the above described consideration that p_a decreases and C_{min} increases as the overall stability of the unimodal characteristics decreases. A threshold of instability p_a/C_{min} value for can be assigned at a value within the range of about 0.1 to about 0.4. The indicia of stability p_a/C_{min} for a particular hydrocarbon material can be compared to the threshold of instability p_a/C_{min} . As can be understood for residuum C in Table 4 the p_a/C_{min} has decreased from a value of 0.87 to a value of 0.26. The first value indicative of a relatively stable hydrocarbon material having unimodal characteristics while the second value suggests that the material has acquired some degree of multimodal character, which may include the formation of coke.

Now referring to Table 6, another embodiment of the invention can be an indicia of stability based upon determining the amount of precipitated asphaltenes which are soluble in a solvent having a polarity between that of the precipitating solvent and a solvent which can dissolve the precipitated asphaltenes completely. For the three stripper bottoms, as an example, asphaltenes were precipitated using heptane, although the precipitating solvent can be any solvent having a polarity between that of the precipitating solvent and a solvent which can dissolve the precipitated asphaltenes completely. For example, the precipitated asphaltenes can then be extracted with a second solvent, in the

example cyclohexane, having polarity that is between the precipitating solvent and a polarity which would substantially dissolve the precipitate completely. Other solvents could be used as the second solvent depending on which solvent was used as the precipitating solvent such as pentane, heptane, or heptane: toluene 1:1 (v:v).

5 Table 6. Solubility of Heptane Asphaltenes in Two Solvents with $\delta = 8.2 \text{ (cal/cc)}^{1/2}$

Material	wt.% Heptane Asphaltenes	wt.% Asphaltenes Soluble in:	
		Cyclohexane	Heptane:toluene (1:1) (v:v)
A (525 °F)	11.9	14.0	63.2
10 B (650 °F)	14.2	10.8	52.4
C (700 °F)	22.4	1.8	26.9

As can be understood from Table 6, both hydrocarbon materials A and B are fully soluble in cyclohexane, yet the heptane asphaltenes are only partially soluble. Again, this is due to the associated unimodal nature of these materials. The cyclohexane-soluble components of the asphaltenes can reflect the state of the solubilizing resins in these materials. The disappearance of the cyclohexane-soluble portion of heptane asphaltenes as the stripper bottoms are increasingly heated is illustrated by the data for the stripper bottoms and appears to coincide with acquired multimodal characteristics, including coke formation. As such, an indicia of stability reflects an observed amount of precipitated asphaltenes soluble in the second solvent.

It is interesting to note that the solvent mixture heptane: toluene (1:1)(v:v), which has the same solubility parameter as cyclohexane, $(8.2 \text{ (cal/cc)}^{1/2})$, gives a larger yield of soluble material than cyclohexane from the heptane asphaltenes for each of the three stripper bottoms. A likely explanation is that in addition to the solubility parameter, there is a chromatographic effect due to the presence of toluene in the mixed solvent. Possibly toluene is displacing some associated material from the associated asphaltene complex. Although solubility parameters of mixtures are additive with the volume fractions of the components, chromatographic solubility is not. The relative solubility portion of a stronger chromatographic solvent in a mixture with a weaker one increases

the overall chromatographic solvent strength almost exponentially. This is a plausible explanation of the data in Table 6. This also provides additional evidence for the presence of associated species in a hydrocarbon material having unimodal characteristics.

Again referring to Table 6, another embodiment of the invention can comprise an
 5 indicia of stability_{y,x} be established by determining the weight percent asphaltene soluble in the second solvent (Y) to the weight of the asphaltene precipitated by the first solvent (X). A larger weight percent asphaltene would indicate a greater coking tendency, as would a smaller weight percent soluble portion of the asphaltene. A threshold of instability_{y,x} can be assigned a value of between about 0.0 to about 1.0. The
 10 indicia of stability_{y,x} can be compared to the threshold of instability_{y,x} to determine the proximity of a hydrocarbon material to acquiring multimodal characteristics.

The ratio values for the three stripper bottoms are 1.2, 0.76, and 0.08 for the materials treated at 273, 343, and 371 °C (525, 650, and 700 °F), respectively. The proximity of the hydrocarbon to acquiring multimodal characteristics, including coke formation, is
 15 closer as the value for this indicia of stability approaches zero.

To further define aspects of the unimodal character of hydrocarbon materials, and illustrate the universal applicability of the above-described indicia of stability, thresholds of instability, or their application to assessing proximity of the unimodal characteristics to acquisition of multimodal characteristics, including carbon deposition or coke
 20 formation, five additional hydrocarbon materials were evaluated. These petroleum residua were Boscan, California Coastal, MaxCL, Redwater, B.C., and Vistar. While these particular residua were the focus of the following examples, their choice is not intended to limit the application of the described embodiments of the invention solely to such hydrocarbon materials. Embodiments of the invention may have application over a
 25 broad range of hydrocarbon materials such as other petroleum residua, heavy oils, coal tars, shale oils, asphalts, or the like.

Now referring to Figures 8 and 9, and Tables 7 and 8, indicia of stability_{pa,Cmin}, and indicia of stability_{y,x} from the cyclohexane soluble portions of precipitated asphaltene for the five hydrocarbon materials are illustrated. For these determinations, hydrocarbon
 30 materials were pyrolyzed at 400 °C for 60 and 90 minutes. Pyrolysis experiments were conducted in a stainless steel reactor, which was a 12 inch diameter, 12 foot long, horizontal steel pipe charged with about 12 g of hydrocarbon material. The reactor was heated

the desired set point temperature (400 °C) and held at that temperature for the duration of the experiment. At the end of the experiment, the reactor was allowed to cool and the contents of the reactor were recovered. The carbon solids or coke can be separated from the product oil by solubility in toluene.

- 5 The amount of carbon solids formed at both 60 and 90 minute residence times was evaluated in terms of the above mentioned indica of stability. Heithaus titrations could not be performed on the 90 minute pyrolysis products because of sample instability and the immediate formation of precipitate in the titration cells. Therefore, the p_a/C_{min} embodiment of indica of instability was not determined for the 90 minute products.

Table 7. Heithaus Titration Results and p_a/C_{min} Indicia of Stability

	Material	p_a	p_o	P	C_{min}	p_a/C_{min}
	Redwater, B.C.					
5	Original	0.698	0.749	2.48	0.676	1.0
	Pyrolyzed 60 min.	0.422	0.753	1.30	3.19	0.13
	Pyrolyzed 90 min.	0.162	0.878	1.05	21.1	0.0076
	CA Coastal					
10	Original	0.614	1.12	2.89	0.529	1.2
	Boscan					
	Original	0.691	0.992	3.21	0.452	1.5
	Pyrolyzed 60 min.	0.245	0.905	1.20	5.00	0.049
15	Pyrolyzed 90 min.	0.285	0.717	1.00	434	0.00
	MaxCL					
	Original	0.682	0.758	2.38	0.725	0.94
	Pyrolyzed 90 min.	0.152	0.973	1.15	6.80	0.022
	Vistar					
20	Original	0.616	0.916	2.38	0.722	0.85
	Pyrolyzed 60 min	0.373	0.831	1.32	3.08	0.12

As can be understood from Figure 8, as indicia of stability p_a/C_{min} approaches about 0.1
 25 the unimodal character of the hydrocarbon material becomes unstable which may be
 accompanied by carbon deposition or coke formation.

Table 8. Heptane Asphaltenes and Asphaltenes Soluble in Cyclohexane

Weight Percent				
	X: Heptane	Y: Asphaltenes		Wt.%
5				Toluene
	Residuum	Asphaltenes: ^a	Soluble in Cyclohexane	Y/X
				Insolubles (Coke)
	Redwater, B.C.			
	Original	11.7	41.4	3.5
10	Pyrolyzed			<0.01
	60 min.	15.9	14.7	0.2
	90 min.	17.1	6.0	2.9
	CA Coastal			
	Original	19.7	23.1	1.2
15	Pyrolyzed			<0.01
	60 min.	13.9	4.5	0.32
	90 min.	11.6	5.7	4.4
	Boscan			7.9
	Original	19.8	40.6	2.1
20	Pyrolyzed			<0.01
	60 min.	15.6	5.3	0.34
	90 min.	12.5	2.6	7.5
	MaxCL			11.2
	Original	18.1	45.8	2.5
25	Pyrolyzed			<0.01
	90 min	19.8	3.6	0.18
	7.0			
	Original			

Pyrolyzed

60 min.	18.2	13.2	0.73	0.2
90 min.	9.5	3.8	0.40	6.2

5 a. Weight percent of toluene soluble material

Similarly it can be understood from Figure 9, that indicia of stability, (weight percent of precipitated asphaltenes soluble in cyclohexane to asphaltenes soluble in heptane) (although other solvent pairs can be used as discussed above) approaches about 1.0 the hydrocarbon material becomes unstable which may be accompanied by carbon deposition or coke formation.

The plots dramatically illustrate the diagnostic potential of the indicia of stability and indicia of instability in measuring how close a hydrocarbon material may be to acquiring multimodal characteristics including carbon deposition such as coke formation.

15 Additional relationships, in addition to those described above, have also been considered in evaluating these hydrocarbon materials. As a result additional embodiments of the invention for evaluation of unimodal character of hydrocarbon materials have been delineated. As discussed above and in greater detail below hydrocarbon materials having unimodal characteristics can be considered to be a series of 20 components functionally related by a continuum of polarity in which core materials such as polar asphaltene materials are dispersed in a solvent phase.

Extensive experimentation was conducted to create a theoretical model to analyze unimodal characteristics related to hydrocarbon material and their transition to multimodal characteristics. The experimentation was also directed to elucidate aspects 25 of the theoretical model for unimodal character which could be practically measured or valued. The model focuses upon association of components in hydrocarbon materials. Resins and solvent layers associated about a core material of hydrocarbon materials such as asphaltene (although the core material may be other polar components of hydrocarbon materials or may include other components associated with the asphaltene), and solvated 30 core materials interacting with each other in an ordered hydrocarbon material system.

The model defines a hydrocarbon solvation shell magnitude term K ($K = K_1 + K_2$).

representing the amount of solvent adsorbed around a core material such as an asphaltene (K_s) or the solvent associated with or trapped by a group of solvated core materials (K_F) in an ordered unimodal system. For hydrocarbon materials such as the petroleum residua evaluated, K values ranging from 3-6 at 25°C can be typical. As a hydrocarbon material is heated K decreases, indicating a decreasing amount of trapped solvent associated with the solvated core materials in the hydrocarbon material and flocculation of the core material may result. This may be a reversible process on cooling, unless pyrolysis reactions begin, at temperatures above 340 °C. Solvation constants (K) are derived using:

10

$$K_S K_F \equiv K = \frac{1 - \eta_{rel}^{-0.4}}{\chi_a / 1.2}$$

In the equation, K is the overall solvation constant for the hydrocarbon material, K_s is the ratio of the size of the solvated core material to the size of the core material itself, K_F is the amount of solvent otherwise associated with the solvated core materials, χ_a is the mass fraction of heptane asphaltenes, divided by an assumed density of 1.2 grams per cubic centimeter to yield the size fraction of the core materials, and η_{rel} is the relative viscosity. To estimate relative viscosities, core material precipitation with can be performed with a solvent such as heptane. Zero shear viscosities (η , cps) are measured for a hydrocarbon material and for the corresponding heptane maltenes (η^0 , cps). The ratio of η/η^0 is called the relative viscosity (η_{rel}) and is diagnostic of the manner in which core materials such as asphaltenes are suspended in a solution of maltenes. This value is somewhat dependent on the solvent used to precipitate the asphaltenes and is related to the state of peptization. A higher relative viscosity indicates a more significant unimodal characteristic. The effective core material volume fraction, ϕ_{eff} is given by multiplying K by the volume fraction of heptane asphaltenes.

$$\phi_{eff} = K \chi_a / 1.2$$

Values of K for hydrocarbon materials can indicate whether a unimodal or bimodal character is present. The value of K_s can depend on the experimental data used. For

example, relative viscosities using heptane or iso-octane maltenes may vary somewhat. Results from the determination of K_S using more than one approach, for a wide selection of hydrocarbon materials having unimodal characteristics, show that for unpyrolyzed hydrocarbon material such as petroleum residua the typical value of K_S is 1.6. With
 5 pyrolysis ($>340^\circ\text{C}$), there is a carbon deposition or coke induction period during which a multimodal system begins to form as discussed by Schabron, J.F., A.T. Pauli, and J.F. Rovani, Jr., *Petroleum Residua Solubility Parameter/Polarity Map: Stability Studies of Residua Pyrolysis*. WRI Report 99-R004 to DOE under Cooperative Agreement DE-FC26-98FT40322 (1999), hereby incorporated by reference. With continued pyrolysis,
 10 carbon deposition or coke begins to form as the unimodal characteristics have broken down irreversibly. When this occurs, relative viscosity measurements have no validity. Thus, to estimate K_F and K_S for pyrolyzed hydrocarbon materials, alternative calculations can be used. In these equations, χ_{cy}

$$K_S = \frac{1}{1 - \chi_{cy}} \qquad K_F = \frac{1}{1 - p_a}$$

is the weight fraction of heptane asphaltenes soluble in cyclohexane, and p_a is the
 15 Heithaus parameter, each as described above.

Now referring to Figures 10, 11, and 12, and Table 9, the theoretical basis for additional embodiments of the invention becomes evident when values for these terms are determined before and after pyrolysis at various severities. Table 9 lists the values of K_S , K_F , and K and weight percent carbon deposition or coke for the five residua. The
 20 data are plotted in Figures 10, 11, 12, respectively.

Table 9. K_S , K_F , and K values for the Original and Pyrolyzed Residua

Residuum		$K_S = (1/(1-\chi_{cy}))$	$K_t = (1/(1-p_d))$	$K = K_S \cdot K_t$	Toluene Insolubles (Coke) ^a
5	Redwater, B.C.				
	Original	1.7	3.3	5.6	<0.01
	Pyrolyzed				
	60 min.	1.2	1.7	2.0	0.2
10	90 min.	1.1	1.2	1.3	2.9
	CA Coastal				
	Original	1.3	2.6	3.4	<0.01
	Pyrolyzed				
	60 min.	1.0	b	-	4.4
15	90 min.	1.1	b	-	7.9
	Boscan				
	Original	1.7	3.2	5.4	<0.01
	Pyrolyzed				
	60 min.	1.1	1.3	1.4	7.5
20	90 min.	1.0	1.4	1.4	11.2
	MaxCL				
	Original	1.8	3.1	5.6	<0.01
	Pyrolyzed				
	90 min	1.0	1.2	1.2	7.0
25	Vistar				
	Original	1.6	2.6	4.2	<0.01
	60 min.				

90 min.

1.0

b

•

6.2

- Weight percent of toluene soluble material
- Heithaus titration not possible due to multi phase product

5 It becomes apparent upon review of the plotted data, that a hydrocarbon material may have sufficient association between components to manifest unimodal characteristics such as a size ratio of the core material to the solvated core material (K_s) when K_s has a value equal to or greater than about 1.1, or a size ratio of a plurality of solvated core materials to other associated solvent (K_F) when K_F has a value equal to or greater than
10 about 1.4, or a sufficient solvation shell (K) when K has a value equal to or greater than about 1.5. For example, hydrocarbon materials having unimodal characteristics may comprise an amount of asphaltenes having polarity, an amount of solvents having lower polarity than the asphaltenes, and a sufficient amount of resins having a polarity intermediate to the polarity of the asphaltenes and the lower polarity of the solvents to
15 establish a solvation shell (K) = ($K_s \cdot K_F$) at a value equal to or greater than about 1.5. These ascertainable measures of the unimodal characteristics of hydrocarbons with respect to K_s , K_F , and K constitute important embodiments of the invention.

As can easily understood, K_s , K_F , and K for a particular hydrocarbon material may be as indicia of stability for the unimodal characteristics of a hydrocarbon material. A first
20 indicia of stability may comprise determining an average size ratio of the solvated core material to the core material itself (indicia of stability $_{K_s}$), or determining an average size ratio of associated solvent around a plurality of solvated core materials to the core material itself (indicia of stability $_{K_F}$), or determining a size ratio of the associated solvent and solvation shell to the core material itself (indicia of stability $_K$). Naturally, these
25 relationships could be expressed in other terms or by the use of other devices and still provide effective indicia of stability.

Naturally, these size ratios may be determined using a variety of instruments such as a nuclear magnetic resonance spectroscopy device, a nuclear magnetic resonance tomography device, a mass spectrometry device, an infrared spectrometry device, a fluorescence device, a light scattering device, a size exclusion chromatography device, a gel electrophoresis device, or a paper chromatography device. The size ratio

may be determined prior to processing of the hydrocarbon material or during processing of the hydrocarbon material. For example, nuclear magnetic resonance imaging has shown that at least two distinct phases are present after pyrolysis with subsequent coke formation.

- 5 It can be further understood that establishing a threshold of instability for unimodal characteristics of hydrocarbon materials may comprise assigning a threshold of instability to size ratios having a value of K_s at about 1.1, or K_f at about 1.4, or K at about 1.5. Below these values the level of association between components in a hydrocarbon material may be insufficient to exhibit unimodal character and transition to
- 10 multimodal character may be initiated including heterogenous mixture formation, carbon deposition, or coke formation. Importantly, various embodiments of the invention allow for comparison of determined indicia of stability to the determined thresholds of instability with respect to K_s , K_f , or K so that the proximity of a particular hydrocarbon material to formation of multimodal characteristics. This may comprise comparing the
- 15 value of K_s for a given hydrocarbon material to the threshold of instability value of K_s . Similarly, the value of K_f for a given hydrocarbon material to the threshold of instability value of K_f , or the value of K for a given hydrocarbon material to the threshold of instability value of K . An approach which was not used prior to the instant invention.

- Another embodiment of the invention can be based upon the free solvent volume of
- 20 the hydrocarbon material. The free solvent volume of hydrocarbon materials having unimodal character relates to the fraction of the total solvent that is not associated with the core materials or associated with or trapped by a plurality of solvated core materials. This indicia of stability can correlate with the amount of initial carbonaceous deposition, including coke formation, below pyrolysis temperatures or the initial amount of
- 25 carbonaceous deposition formed in the early stages of a pyrolytic process. This indicia of stability does not include the amount of carbonaceous deposition when pyrolysis is carried to completion. The total amount of carbonaceous deposition, including deposition of coke, may be estimated by further determining the hydrogen-carbon ratio of the hydrocarbon material. This ratio is subsequently used to calculate the weight of
- 30 the total carbon content of an amount of hydrocarbon material as would be well known to

those with skill in the art. With respect to the average K value, \bar{K} , the method of determining ϕ_{fs} comprises $\phi_{fs} = (1 - K)(1 - p_1)(x_w + x_2)p_1$. The average K is:

unpyrolyzed hydrocarbon material value can be about 1.6. Values for ϕ_{FS} correlate to deposition of carbonaceous material when the value for K_s is held constant. Thus the only measurements which may be required to determine $\phi_{FS} = [1 - K_s (1/1 - p_a) (\chi_a/1.2)]$ in this manner can be the value of weight percent heptane asphaltenes (χ_a) and the value of

5 petizability of asphaltenes (p_a). Other methods of determining free solvent volume, or modifying the values relating structure consideration such as H/C ratio, or fraction of bridge head aromatic carbons may be used, and are encompassed by the invention.

Regarding this embodiment of the invention, the weight percent heptane asphaltenes (χ_a), and the value of petizability of asphaltenes (p_a) may be determined as discussed

10 above. Keeping in mind that the concept can work with other precipitating solvents and other dissolvents as discussed.

The p_a , χ_a , and the ϕ_{FS} for five hydrocarbon materials having unimodal characteristics were determined. The data for these determinations was compiled and provided in Table

10.

15 Table 10. Free Solvent Volumes at 25°C

Residuum	$\chi/1.2$	p_a	ϕ_{ps}^a
Redwater, B.C.	0.097	0.698	0.49
CA Coastal	0.164	.0614	0.32
Boscan	0.165	0.691	0.14
20 MaxCL	0.151	0.682	0.24
Vistar	0.150	0.616	0.38

a. $K_s = 1.6$

The five hydrocarbon materials were pyrolyzed in five (5) gram reactor tubes at 400° C for 90 minutes. The initial amount of carbonaceous deposition,

25 including coke deposition, is set out for each hydrocarbon material in Table 11.

Table 11. Carbonaceous Material in Tube Reactor for 90 Minutes at 400° C

	Residuum	Toluene Insolubles (Coke), Wt. %
	Redwater, B.C.	1.3
	CA Coastal	7.2
	Boscan	10.6
5	MaxCL	8.4
	Vistar	4.3

Now referring to Figure 13, which is a plot of initial deposition of carbonaceous material versus ϕ_{FS} . As can be understood, from the plot as ϕ_{FS} decreases the amount of initial carbonaceous material that forms increases for a given set of processing parameters. As such, an embodiment of the invention provides an indica of stability based upon ϕ_{FS} with respect to predicting the amount of initial carbonaceous deposition. Moreover, plots of initial carbonaceous material formation versus ϕ_{FS} could be generated for any variety of hydrocarbon materials for particular processing conditions, such as different pyrolysis temperatures or for different pyrolysis times or in various combinations, to rank the hydrocarbon materials in terms of relative carbon deposition potential based upon ϕ_{FS} .

As can be further understood additional embodiments of the invention may include selecting distillation parameters to distill hydrocarbon material having unimodal characteristics use predetermined indicia of stability to avoid reaching the threshold of instability. By distilling hydrocarbon material using distillation parameters that take into account or compare the indica of stability to the threshold of stability, prior to or during the distillation process or other processing event, it may be possible to select distillation parameters to allow substantially continuous distillation avoiding the threshold of instability for said unimodal characteristics. Specifically, selecting distillation parameters having predetermined indicia of stability may avoid or limit coke formation. Importantly, a method of processing hydrocarbon material using distillation parameters based upon indicia of stability, indicia of instability, independently or in cooperation, may allow distillation of hydrocarbon materials so as to have ascertainable indicia of stability in closer proximity to the threshold of instability compared to typical distillation parameters. By processing a hydrocarbon material so that the indicia of stability are closer to the threshold of instability in a substantially continuous distillation event, the

output of liquid distillables per unit amount of said hydrocarbon material may be increased by comparison with typical parameters of distillation. As described above, an increase in the amount of liquid distillables from the same amount of hydrocarbon material may decrease the amount of energy used per unit of liquid distillate produced, or
5 may also reduce the amount of emissions generated per unit of liquid distillate produced. Such reduction in emissions may be a reduction in carbon dioxide. Moreover, when hydrocarbon materials are distilled in a continuous distillation event it may increase the purity of at least a portion of said liquid distillates.

Another embodiment of the invention, understandably includes, the selection of
10 hydrocarbon materials for purchase or processing based upon determined indicia of stability for the degree of unimodal characteristics. Naturally, some hydrocarbon materials which have indicia of stability which show a high level of unimodal characteristics may have greater desirability for some parameters of processing.

Alternately, with respect to some embodiments of the invention selecting distillation
15 parameters for hydrocarbon material having unimodal characteristics may be designed to reach a predetermined level of instability characteristics. As such, distilling these hydrocarbon materials using such distillation parameters may continue until reaching said predetermined level of instability characteristics. A method of processing hydrocarbon material in this fashion initiate the formation of a predetermined amount of
20 carbon or coke. Again as above, such distillation parameters may allow for maintaining continuous distillation until reaching the predetermined level of instability characteristics.

Naturally, because products from these processes may be distinguished from conventional processing by their purity an embodiment of the invention comprises the
25 isolation of these higher purity products.

As mentioned earlier, this invention can be embodied in a variety of ways. In addition, each of the various elements of the invention and claims may also be achieved in a variety of manners. This disclosure should be understood to encompass each such variation, be it a variation of an embodiment of any apparatus embodiment, a method or
30 process embodiment, or even merely a variation of any element of these. Particularly, it

words for each element may be expressed in equivalent apparatus terms or method terms

-- even if only the function or result is the same. Such equivalent, broader, or even more generic terms should be considered to be encompassed in the description of each element or action. Such terms can be substituted where desired to make explicit the implicitly broad coverage to which this invention is entitled. As but one example, it should be understood that all action may be expressed as a means for taking that action or as an element which causes that action. Similarly, each physical element disclosed should be understood to encompass a disclosure of the action which that physical element facilitates. Regarding this last aspect, as but one example, the disclosure of a "dissolvent" should be understood to encompass disclosure of the act of "dissolving" -- whether explicitly discussed or not -- and, conversely, were there only disclosure of the act of "dissolving", such a disclosure should be understood to encompass disclosure of a "dissolvent." Such changes and alternative terms are to be understood to be explicitly included in the description.

The foregoing discussion and the claims which follow describe the preferred embodiments of the invention. Particularly with respect to the claims it should be understood that changes may be made without departing from their essence. In this regard it is intended that such changes would still fall within the scope of the present invention. It is simply not practical to describe and claim all possible revisions which may be accomplished to the present invention. To the extent such revisions utilize the essence of the invention each would naturally fall within the breadth of protection accomplished by this patent. This is particularly true for the present invention since its basic concepts and understandings are fundamental in nature and can be applied in a variety of ways to a variety of fields.

Any references mentioned, including but not limited to federal or state statutes, patents, publications, brochures, marketing materials, or inter-net pages, in this patent application, are hereby incorporated by reference or should be considered as additional text or as an additional exhibits or attachments to this application to the extent permitted; however, to the extent statements might be considered inconsistent with the patenting of this/these invention(s) such statements are expressly not to be considered as made by the applicant. Further, the disclosure should be understood to include support for each

various combinations and permutations of each

In addition, unless the context requires otherwise, it should be understood that the term "comprise" or variations such as "comprises" or "comprising", are intended to imply the inclusion of a stated element or step or group of elements or steps but not the exclusion of any other element or step or group of elements or steps. Such terms should

5 be interpreted in their most expansive form so as to afford the applicant the broadest coverage legally permissible in countries such as Australia and the like. Such terms are intended to have an inclusive meaning rather than an exclusive one and should be interpreted in their most expansive form so as to afford the applicant the broadest coverage legally permissible. Therefore, in countries such as Australia and the like, such

10 terms are not intended to have an exclusive, or more limited meaning. Thus, the applicant should be understood to claim at least: i) a molecular weight / polarity map system; ii) each of the coking indexes; iii) a system of pre-distillation evaluation of hydrocarbon material; iv) a nearly continuous distillation system; v) a system for optimizing the yields of distillable liquids; vi) a system for determining the coking indexes; vii) the resulting

15 products; viii) the related methods disclosed and described, ix) similar, equivalent, and even implicit variations of each of these devices and methods; x) those alternative designs which accomplish each of the functions shown as are disclosed and described; xi) those alternative designs and methods which accomplish each of the functions shown as are implicit to accomplish that which is disclosed and described; xii) each feature,

20 component, device, and step shown as separate and independent inventions; xiii) the combinations of applied systems including the designs disclosed, xiv) the resulting products produced by such systems or components, xv) related methods including the techniques of the applied systems, and xvi) the various combinations and permutations of each of the above.

VI. CLAIMS

We claim:

1. A molecular weight - polarity map for hydrocarbon materials having unimodal characteristics comprising:
 - 5 a. a first axis having values relating to molecular weight;
 - b. a second axis having values relating to solubility parameter;
 - c. a plurality of solvent tuned contour lines each defining a solubility parameter range in $(\text{cal/cc})^{1/2}$; and
 - d. a core material solubility region.
- 10 2. A molecular weight - polarity map for hydrocarbon materials as described in claim 1, wherein said core material solubility region comprises between about 6.9 $(\text{cal/cc})^{1/2}$ to about 11.0 $(\text{cal/cc})^{1/2}$.
3. A molecular weight - polarity map for hydrocarbon materials as described in claim 1, wherein said solubility parameter range in $(\text{cal/cc})^{1/2}$ comprises about 0.5 to about 0.6
15 $(\text{cal/cc})^{1/2}$.
4. A molecular weight - polarity map for hydrocarbon materials as described by claim 1, wherein said core material comprises asphaltenes.
5. A molecular weight - polarity map for hydrocarbon materials as described by claim 1, wherein a first solvent tuned contour line comprises an iso-octane tuned contour line.
- 20 6. A molecular weight - polarity map for hydrocarbon materials as described by claim 5, wherein a second solvent tuned contour line comprises a heptane tuned contour line.
7. A molecular weight - polarity map for hydrocarbon materials as described by claim 6, wherein a third solvent tuned contour line comprises a heptane:toulene (2:1) (v:v) tuned

8. A molecular weight - polarity map for hydrocarbon materials as described by claim 7, wherein a fourth solvent tuned contour line comprises a heptane:toulene (1:2) (v:v) tuned contour line.
9. A molecular weight - polarity map for hydrocarbon materials as described by claim 8, wherein a fifth solvent tuned contour line comprises a toulene tuned contour line.
10. A molecular weight - polarity map for hydrocarbon materials as described by claim 9, wherein a sixth solvent tuned contour line comprises a toluene:carbon disulfide (55:45) (v:v) tuned contour line.
11. A molecular weight - polarity map for hydrocarbon materials as described by claim 10, wherein a seventh solvent tuned contour line comprises a carbon disulfide tuned contour line.
12. A molecular weight - polarity map for hydrocarbon materials as described by claim 1, further comprising molecular weight - polarity coordinate locations of said core materials.
13. A molecular weight - polarity map for hydrocarbon materials as described by claim 12, wherein said molecular weight - polarity coordinate locations of said core materials relate to at least one unimodal characteristic.
14. A molecular weight - polarity map for hydrocarbon materials as described by claim 13, wherein said at least one unimodal characteristic comprises a variably adjustable core material having a molecular weight responsive to temperature change.
15. A molecular weight - polarity map for hydrocarbon materials as described by claim 13, wherein said at least one unimodal characteristic comprises a core material having a polarity stabilizer function responsive to temperature change.
16. A molecular weight - polarity map for hydrocarbon materials as described by claim

14, wherein variably adjustable core material comprises a core material that decreases in molecular weight in response to an increase in temperature.

17. A method of processing hydrocarbon material, comprising the steps of:

- a. providing an amount of said hydrocarbon material having at least one unimodal
5 characteristic; and
- b. determining at least one indicia of stability based on said at least one unimodal characteristic.

18. A method of processing hydrocarbon material as described in claim 17, further comprising the steps of:

- 10 a. establishing at least one threshold of instability of said at least one unimodal characteristic;
- b. comparing said at least one indicia of stability to said at least one threshold of instability; and
- c. assessing the proximity of said at least one unimodal characteristic to forming a
15 multimodal characteristic.

19. A method of processing hydrocarbon material as described in claim 17, wherein having said at least one unimodal characteristic comprises ascertaining an average size ratio of a solvated core material size to a core material size (K_s), wherein K_s has a value equal to or greater than about 1.1.

20

20. A method of processing hydrocarbon material as described in claim 17, wherein having said at least one unimodal characteristic comprises ascertaining an average size ratio of solvent associated with a plurality of solvated core materials to said plurality of solvated core materials (K_F), wherein K_F has a value equal to or greater than about 1.4.

25

21. A method of processing hydrocarbon material as described in claim 17, wherein having said at least one unimodal characteristic comprises ascertaining a solvation shell

22. A method of processing hydrocarbon material as described in claim 17, wherein having said at least one unimodal characteristic comprises:
- a. maintaining an amount of asphaltenes having polarity;
 - b. maintaining an amount of solvents having lower polarity than said asphaltenes; and
 - 5 c. maintaining a sufficient amount of resins having a polarity intermediate to said polarity of said asphaltenes and to said lower polarity of said solvents to establish a value of said solvation shell $(K) = (K_s \cdot K_F)$ equal to or greater than about 1.5.

23. A method of processing hydrocarbon material as described in claim 17, wherein said step of providing an amount of hydrocarbon material further comprises the step of
- 10 selecting said hydrocarbon material from the group consisting of coal tars, shale oils, tar sand bitumen, asphalts, heavy oils, and petroleum residua.

24. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining at least one indicia of stability based on said at least one unimodal characteristic comprises determining a value of K_s of said hydrocarbon
- 15 material, wherein $K_s = K_s = (1/(1-\chi_{cy}))$.

25. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining at least one indicia of stability based on said at least one unimodal characteristic comprises determining a value of K_F of said hydrocarbon material, wherein $K_F = K_F = (1/(1-p_a))$.

- 20 26. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining at least one indicia of stability based on said at least one unimodal characteristic comprises determining a value of K of said hydrocarbon material, wherein $K = K_s \cdot K_F$, and wherein $K_s = K_s = (1/(1-\chi_{cy}))$, and wherein $K_F = K_F = (1/(1-p_a))$.

- 25 27. A method of processing hydrocarbon material as described in claim 24, wherein determining said value of K_s of said hydrocarbon material using nuclear magnetic

resonance, wherein absorption of electromagnetic radiation by said solvated core material and absorption of electromagnetic radiation by said core material are analyzed to ascertain said average size ratio K_s .

28. A method of processing hydrocarbon material as described in claim 25, wherein
5 determining at least one indicia of stability for said unimodal characteristics comprises determining said value of K_F of said hydrocarbon material using nuclear magnetic resonance, wherein absorption of electromagnetic radiation by said solvent associated with said solvated core materials and absorption of electromagnetic radiation by said plurality of solvated core materials are analyzed to ascertain said average size ratio K_F .
- 10 29. A method of processing hydrocarbon material as described in claim 26, wherein determining at least one indicia of stability for said unimodal characteristics comprises determining a value of $K = K_s \cdot K_F$ of said hydrocarbon material using magnetic resonance, wherein absorption of electromagnetic radiation by said solvated core material and absorption of electromagnetic radiation by said core material are analyzed to
15 ascertain said average size ratio K_s , and wherein absorption of electromagnetic radiation by said solvent associated with said solvated core materials and absorption of electromagnetic radiation by said plurality of solvated core materials are analyzed to provide said average size ratio K_F .
30. A method of processing hydrocarbon material as described in claim 18, wherein
20 establishing a threshold of instability based on said at least one unimodal characteristics comprises assigning a value of about 1.1 to a threshold of instability K_s .
31. A method of processing hydrocarbon material as described in claim 18, wherein establishing a threshold of instability based on said at least one unimodal characteristic comprises assigning a value of about 1.4 to a threshold of instability K_F .
- 25 32. A method of processing hydrocarbon material as described in claim 18, wherein establishing a threshold of instability based on said at least one unimodal characteristic comprises assigning a value of about 1.7 to a threshold of instability K .

33. A method of processing hydrocarbon material as described in claim 18, wherein said step of comparing said indicia of stability to said threshold of instability comprises comparing a determined value of K_s of said hydrocarbon material to said value of about 1.1 assigned to said threshold of instability K_s .
- 5 34. A method of processing hydrocarbon material as described in claim 18, wherein said step of comparing said indicia of stability to said threshold of instability comprises comparing a determined value of K_F of said hydrocarbon material to said value of about 1.4 assigned to said threshold of instability K_F .
35. A method of processing hydrocarbon material as described in claim 18, wherein
10 said step of comparing said indicia of stability to said threshold of instability comprises comparing a determined value of K of said amount of said hydrocarbon material to said value of about 1.5 assigned to said threshold of instability K .
36. A method of processing hydrocarbon material as described in claims 19, 20, 21, 24,
25, 26, 27, 28, or 29, further comprising the step of using a hydrocarbon material
15 analysis device to determine said size ratio selected from the group consisting of a nuclear magnetic resonance device, a nuclear magnetic resonance spectroscopy device, a nuclear magnetic resonance tomography device, a mass spectrometry device, an infrared spectrometry device, a raman spectroscopy device, a size exclusion chromatography device, a gel electrophoresis device, and paper chromatography device.
- 20 37. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining indicia of stability for said unimodal characteristics comprises:
a. providing a hydrocarbon material component analysis device;
b. calibrating said hydrocarbon material component analysis device;
c. mixing an amount of hydrocarbon material in a precipitating solvent;
25 d. precipitating asphaltenes from said hydrocarbon material;
e. extracting maltenes into said precipitating solvent;
f. determining an amount of at least one unimodal characteristic stability component of said hydrocarbon material;

said maltenes.

38. A method of processing hydrocarbon material as described in claim 37, wherein said step of providing a hydrocarbon material component analysis device comprises selecting said hydrocarbon material component analysis device from the group consisting of a nuclear magnetic resonance spectroscopy device, a nuclear magnetic resonance tomography device, a mass spectrometry device, an infrared spectrometry device, a microscope device, an infrared raman spectroscopy device, a size exclusion chromatography device, a gel electrophoresis device, and a paper chromatograph device.

39. A method of processing hydrocarbon material as described in claim 37, wherein said step of calibrating said hydrocarbon material component analysis device comprises identifying characteristics of polystyrene having known molecular weight.

40. A method of processing hydrocarbon material as described in claim 39, wherein said precipitating solvent comprises iso-octane.

41. A method of processing hydrocarbon material as described in claim 40, wherein said step of analyzing said maltenes with said hydrocarbon material component analysis device comprises:
a. separating said maltenes with said size exclusion chromatography device; and
b. comparing elution volumes of said maltenes to elution volumes of said components of polystyrene having known molecular weight.

42. A method of processing hydrocarbon material as described in claim 41, wherein determining an amount of said at least one unimodal characteristic stability component in said maltenes comprises detecting an apparent molecular weight of said at least one unimodal characteristic stability component.

43. A method of processing hydrocarbon material as described in claim 42, wherein determining an amount of said at least one unimodal characteristic stability component comprises observing elution of said at least one unimodal

characteristic stability component corresponding to a leading edge high molecular weight shoulder component.

44. A method of processing hydrocarbon material as described in claim 43, wherein said leading edge high molecular weight component has an apparent molecular weight
5 about equal to or greater than about 500 gram per mole.

45. A method of processing hydrocarbon material as described in claim 17, wherein said step of determining indicia of stability based on said at least one unimodal characteristic comprises:

- a. providing a titration device;
- 10 b. mixing an amount of said hydrocarbon material into an amount of aromatic dissolvent (V_s);
- c. titrating dissolvent soluble components in said amount of aromatic dissolvent with an amount of weak aliphatic solvent until a flocculent forms (V_t);
- d. calculating the flocculation ratio at infinite dilution (FR_{max}), wherein $FR_{max} = V_s / (V_s$
15 $+ V_t)$, and wherein V_s has a value about equal to said volume of dissolvent, and wherein V_t has a value about equal to said amount of weak solvent;
- e. determining the dilution concentration at zero titrant level (C_{min}), wherein $C_{min} = W_a / (V_s + V_t)$, and wherein W_a has a value about equal to said amount of said hydrocarbon material;
- 20 f. determining the peptizability of asphaltenes determining (p_a), wherein $p_a = 1 - FR_{max}$; and
- g. determining a value of p_a / C_{min} for said amount of toluene soluble components.

46. A method of processing hydrocarbon material as described in claim 45, wherein said step of mixing an amount of said hydrocarbon material into an amount of aromatic
25 dissolvent (V_s) comprises mixing said amount of said hydrocarbon material into an amount of toluene.

said step of titrating dissolvent soluble components in said amount of aromatic dissolvent

with an amount of weak aliphatic solvent until a flocculent forms (V_f) comprises titrating said dissolvent soluble components in said volume of aromatic dissolvent with an amount of iso-octane.

48. A method of processing hydrocarbon material as described in claim 18, wherein
 5 said step of establishing a threshold of instability based on said at least one unimodal characteristic comprises assigning a value within the range of about 0.1 to about 0.4 to a threshold of instability p_a / C_{min} .

49. A method of processing hydrocarbon material as described in claim 48, wherein
 10 said step of comparing said indicia of stability to said threshold of instability comprises comparing said determined value of p_a / C_{min} of said hydrocarbon material to said value of about 0.1 to about 0.4 assigned to said threshold of instability p_a / C_{min} .

50. A method of processing hydrocarbon material as described in claim 17, wherein
 said step of determining indicia of stability based on said at least one unimodal characteristic comprises:

- 15 a. precipitating an amount of asphaltenes_x from an amount of said hydrocarbon material with a first solvent;
- b. extracting precipitated asphaltenes_x with a second solvent, wherein said second solvent has a polarity between a polarity of said first solvent and a polarity of a third solvent capable of substantially dissolving said asphaltenes_x completely; and
- 20 c. determining an amount of asphaltenes_y soluble in said second solvent.

51. A method of processing hydrocarbon material as described in claim 50, wherein
 said step of precipitating an amount of asphaltenes_x from an amount of said hydrocarbon material with a first solvent further comprises the step of selecting said first solvent from the group consisting of iso-octane, pentane, hexane, and heptane.

25 52. A method of processing hydrocarbon material as described in claim 51, wherein
 said step of extracting precipitated asphaltenes_x with a second solvent comprises selecting said second solvent has polarity between the polarity of said first solvent and a polarity of

third solvent capable of substantially dissolving said asphaltenes, completely further comprises the step of selecting said second solvent from the group consisting of cyclohexane, pentane, hexane, heptane, and heptane:toluene (1:1) (v:v).

53. A method of processing hydrocarbon material as described in claim 18, wherein
5 said step of establishing a threshold of instability based on said at least one unimodal characteristic comprises assigning a value of equal to or less than about 0.2 weight percent to a threshold of instability γ .

54. A method of processing hydrocarbon material as described in claim 18, wherein
10 said step of determining indicia of stability based on said at least one unimodal characteristic comprises weight percent asphaltenes_y soluble in said second solvent over weight percent asphaltenes_x precipitated by said first solvent.

55. A method of processing hydrocarbon material as described in claim 2 wherein said
step of establishing a threshold of instability based on said at least one unimodal
characteristic comprises assigning a value between about 0.0 to about 1.0 to a threshold
15 of instability_{x/y}.

56. A method of processing hydrocarbon material as described in claims 18, 24, 34, 35,
42, 43, 44, 49, 53, or 54, further comprising the step of predicting the proximity of said
hydrocarbon material to coke formation.

57. A method of processing hydrocarbon material as described in claim 17, wherein
20 said step of determining indicia of stability based on said at least one unimodal characteristic comprises determining free solvent volume.

58. A method of processing hydrocarbon material as described in claim 57, wherein
determining said free solvent volume comprises determining an amount of unassociated
solvent in said hydrocarbon material, wherein said unassociated solvent does not solvate
the asphaltene core materials, and wherein the amount of unassociated solvent is determined by
purifying of solvated core materials

59. A method of processing hydrocarbon material as described in claim 57, wherein determining said free solvent volume comprises determining $\phi_{FS} = 1 - K_s (1/1 - p_a) (\chi_a/1.2)$, wherein K_s has a value of about 1.6.

60. A method of processing hydrocarbon material as described in claim 56, wherein
- 5 determining said free solvent volume comprises:
 - a. providing a titration device;
 - b. mixing an amount of said hydrocarbon material into an amount of aromatic dissolvent (V_s);
 - c. titrating dissolvent soluble components in said amount of aromatic dissolvent with an
 - 10 amount of weak aliphatic solvent until a flocculent forms (V_l);
 - d. calculating the flocculation ratio at infinite dilution (FR_{max}), wherein $FR_{max} = V_s / (V_s + V_l)$, and wherein V_s has a value about equal to said amount of aromatic dissolvent, and wherein V_l has a value about equal to said amount of weak aliphatic solvent;
 - e. determining the peptizability of asphaltenes p_a , wherein $p_a = 1 - FR$;
 - 15 f. precipitating an amount of asphaltenes from an amount of said hydrocarbon material with a precipitating solvent;
 - g. determining the mass fraction asphaltenes (χ_a); and
 - h. determining ϕ_{FS} , wherein $\phi_{FS} = 1 - K_s (1/1 - p_a) (\chi_a/1.2)$.

61. A method of processing hydrocarbon material as described in claim 60, wherein

- 20 said step of mixing an amount of said hydrocarbon material into an amount of aromatic dissolvent (V_s) further comprises selecting said aromatic dissolvent from the group consisting of toluene, benzene, xylene, and ethylbenzene.

62. A method of processing hydrocarbon material as described in claim 60, wherein

- 25 said step of titrating dissolvent soluble components in said amount of aromatic dissolvent with an amount of weak aliphatic solvent until a flocculent forms (V_l) further comprises selecting said aliphatic solvent from the group consisting of iso-octane, pentane, hexane, and hexadecane.

63. A method of processing hydrocarbon material as described in claim 57, wherein

said step of precipitating an amount of asphaltenes from an amount of said hydrocarbon material with a precipitating solvent further comprises the step of selecting said precipitating solvent from the group consisting of iso-octane, pentane, hexane, and heptane.

5 64. A method of processing hydrocarbon material as described in claim 57, further comprising the step of determining an initial amount of coke formation when exceeding said threshold of instability .

65. A method of processing hydrocarbon material as described in claims 17, 18, 33, 34, 35, 37, 41, 44, 45, 46, 47, 49, 50, 53, 54, 55, 57, 59, 60, or 64, further comprising the
10 steps of:

- a. selecting distillation parameters to distill said hydrocarbon material having unimodal characteristics, wherein said distillation parameters have predetermined indicia of stability to avoid reaching said threshold of instability;
- b. distilling said hydrocarbon material using said distillation parameters; and
- 15 c. avoiding the threshold of instability for said unimodal characteristics.

66. A method of processing hydrocarbon material as described in claim 65, wherein said step of selecting distillation parameters to distill said hydrocarbon material having unimodal characteristics, wherein said distillation parameters have predetermined indicia
20 of stability to avoid reaching said threshold of instability comprises selecting distillation parameters having predetermined indicia of stability to avoid coke formation.

67. A method of processing hydrocarbon material as described in claim 61, further comprising the step of maintaining continuous distillation until reaching said predetermined indicia of stability to avoid coke formation.

25 68. A method of processing hydrocarbon material as described in claim 67, wherein said step of distilling said hydrocarbon material using said distillation parameters
comprising the step of maintaining continuous distillation until reaching said predetermined indicia of stability in closer proximity to said threshold of instability compared to typical

distillation parameters.

69. A method of processing hydrocarbon material as described in claims 17, 18, 33, 34, 35, 37, 41, 44, 45, 46, 47, 49, 50, 53, 54, 55, 57, 59, 60, or 64 further comprising the steps of:

- 5 a. selecting distillation parameters for said hydrocarbon material having unimodal characteristics to reach a predetermined level of instability characteristics;
- b. distilling said hydrocarbon material using said distillation parameters; and
- c. continuing said hydrocarbon material until reaching said predetermined level of instability characteristics.

10 70. A method of processing hydrocarbon material as described in claim 69, wherein said step of reaching said predetermined level of instability comprises initiating a predetermined amount of coke.

71. A method of processing hydrocarbon material as described in claim 70, further comprising the step of maintaining continuous distillation until reaching said
15 predetermined level of instability characteristics.

72. A method of processing hydrocarbon material as described in claim 71, further comprising the step of determining the hydrogen-carbon ratio of said hydrocarbon material.

73. A method of processing hydrocarbon material as described in claim 72, further
20 comprising the step of determining a total amount of coke which may form from said hydrocarbon material.

74. A method of processing hydrocarbon material as described in claim 68, further comprising the step of increasing output of liquid distillate per unit amount of said hydrocarbon material.

75. A method of processing hydrocarbon material as described in claim 68, further

comprising the step of decreasing the amount of energy used per unit of liquid distillate produced.

76. A method of processing hydrocarbon material as described in claim 68, further
5 comprising the step of reducing the amount of emissions generated per unit of liquid distillate produced.

77. A method of processing hydrocarbon material as described in claim 76, wherein said step of reducing the amount of emissions generated per unit of liquid distillate produced comprises reducing carbon dioxide emissions.

10 78. A method of processing hydrocarbon material as described in claim 68, further comprising the step of increasing the purity of at least a portion of said liquid distillates.

79. A method of processing hydrocarbon material as described in claim 17, 18, 33, 34, 35, 37, 41, 44, 45, 46, 47, 49, 50, 53, 54, 55, 57, 59, 60, or 64, further comprising the step of selecting said hydrocarbon material to process based upon said indica of stability
15 for said unimodal characteristics.

80. A method of processing hydrocarbon material as described in claim 36, further comprising the step of selecting said hydrocarbon material to process based upon said indica of stability for said unimodal characteristics.

81. Liquid distillate produced in accordance with the process of claim 65.

20 82. Liquid distillate produced in accordance with the process of claim 68.

83. Liquid distillate produced in accordance with the process of claim 69.

84. Liquid distillate produced in accordance with the process of claim 71.

... hydrocarbon material comprising

- a. an amount of core material having polarity;
 - b. an amount of solvents having lower polarity than said core material; and
 - c. an amount of resins having a polarity intermediate to said polarity of said core material and to said lower polarity of said solvents sufficient to establish at least one
- 5 unimodal characteristic.

86. A hydrocarbon material as described in claim 85, wherein said at least one unimodal characteristic comprises a value of a solvation shell (K), and wherein $K = (K_s \cdot K_F)$ has a value equal to or greater than about 1.5.

87. A hydrocarbon material as described in claim 85, wherein said at least one unimodal

10 characteristic comprises a value of an average size ratio of a solvated core material size to a core material size (K_s), wherein K_s has a value equal to or greater than about 1.1.

88. A hydrocarbon material as described in claim 85, wherein said at least one unimodal characteristic comprises a value of an average size ratio of solvent associated with a

15 plurality of solvated core materials to said plurality of solvated core materials (K_F), wherein K_F has a value equal to or greater than about 1.4.

89. A hydrocarbon material as described in claim 85, wherein said core material comprises asphaltenes.

90. A hydrocarbon material as described in claim 85, wherein said hydrocarbon material

20 has an indicia of stability based on said at least one unimodal characteristic which has a value outside the range naturally occurring hydrocarbon materials.

91. A hydrocarbon material as described in claim 85, further comprising a level of purity greater than naturally occurring hydrocarbon materials.

92. Methods substantially as described hereinbefore and with reference to any of the

accompanied examples.

93. Apparatuses substantially as described hereinbefore and with reference to any of the accompanying examples.

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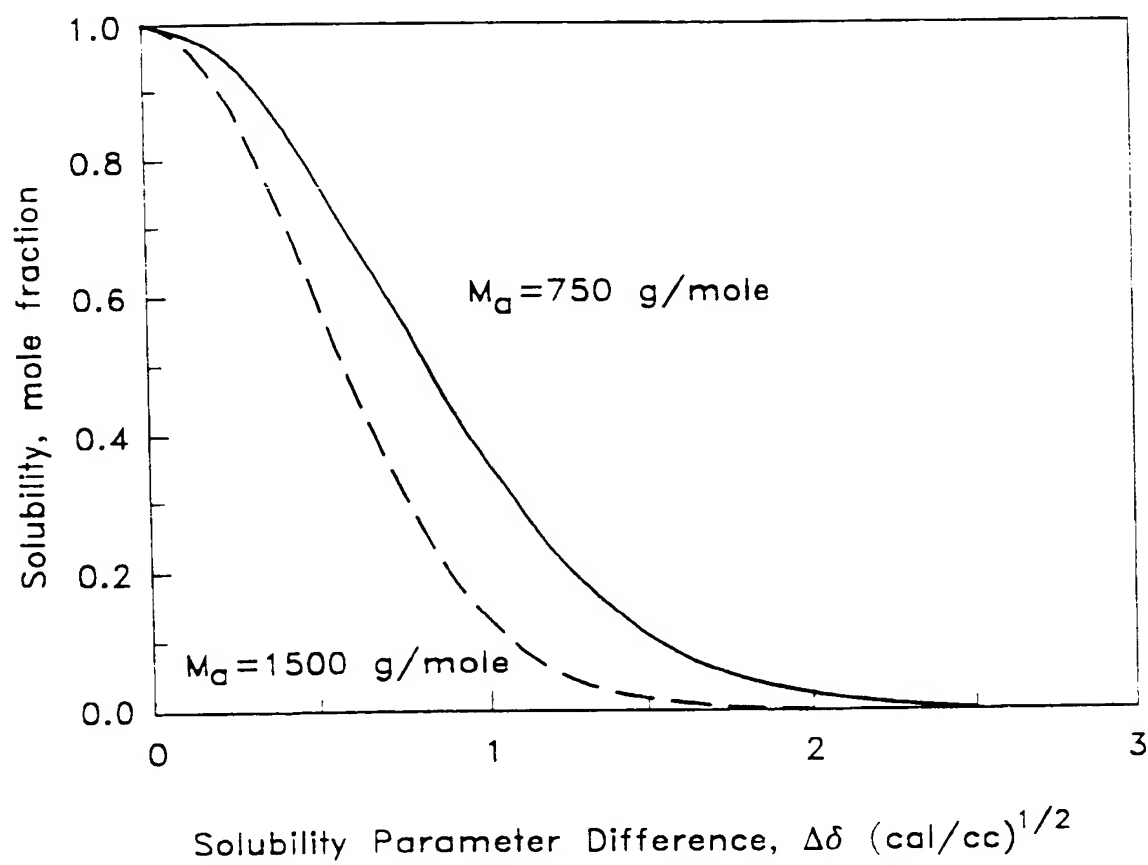


Fig. 1

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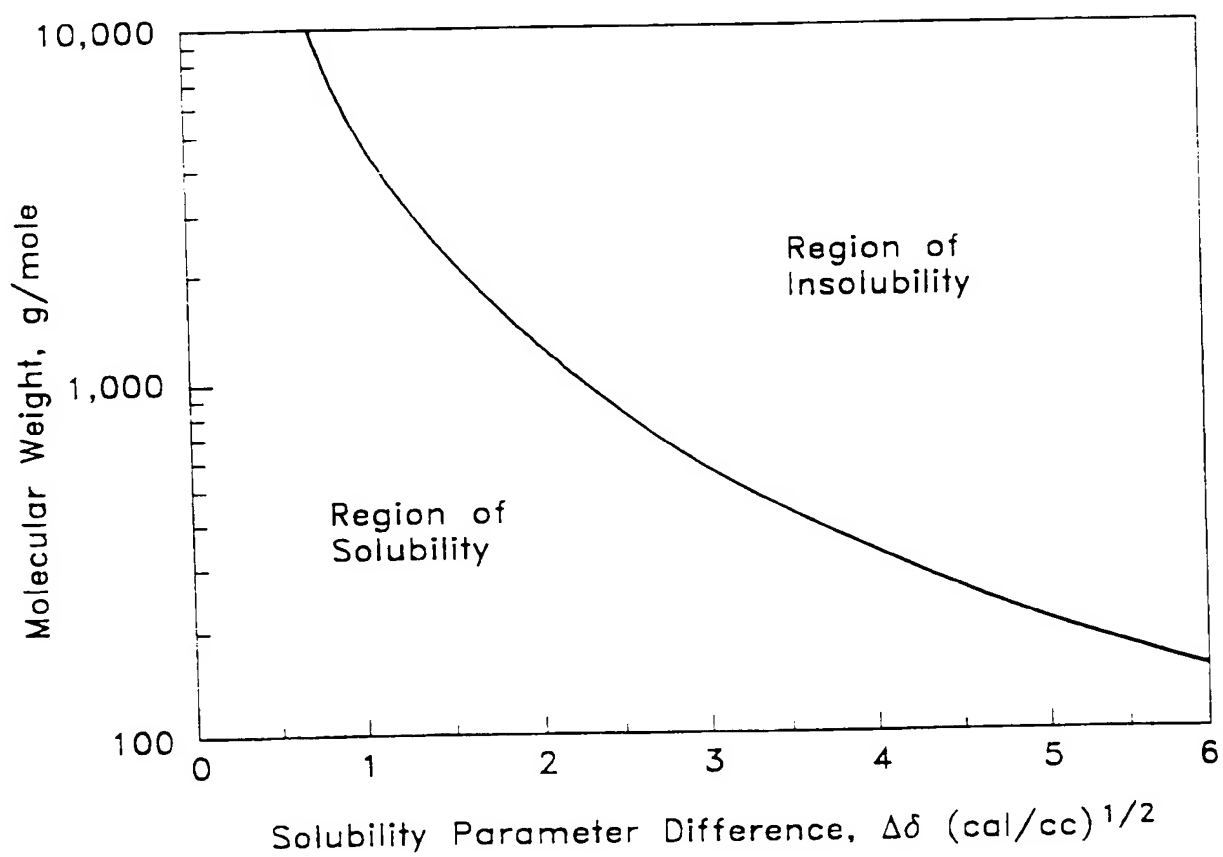


Fig. 2

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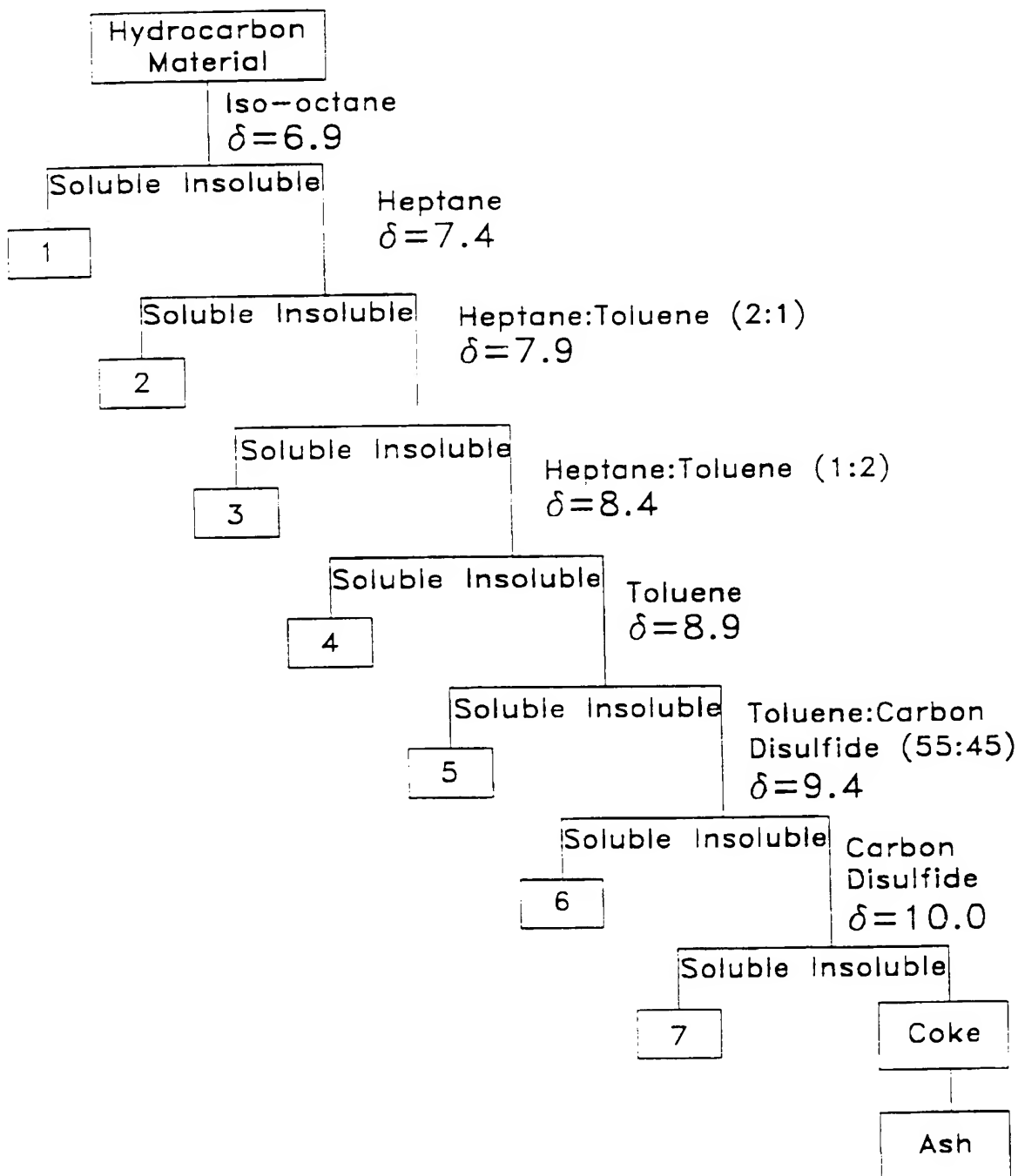


Fig. 3

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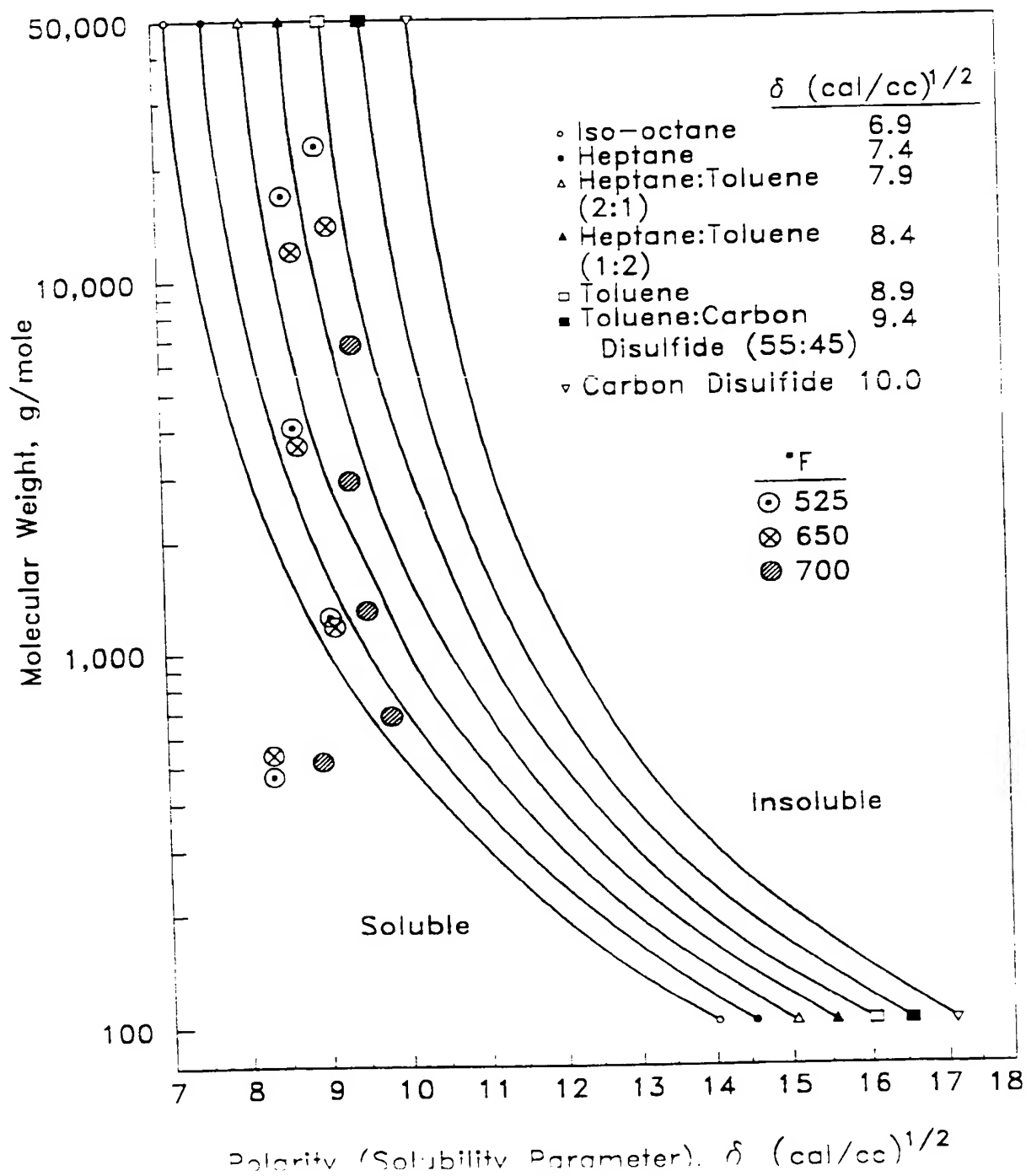


Fig. 4

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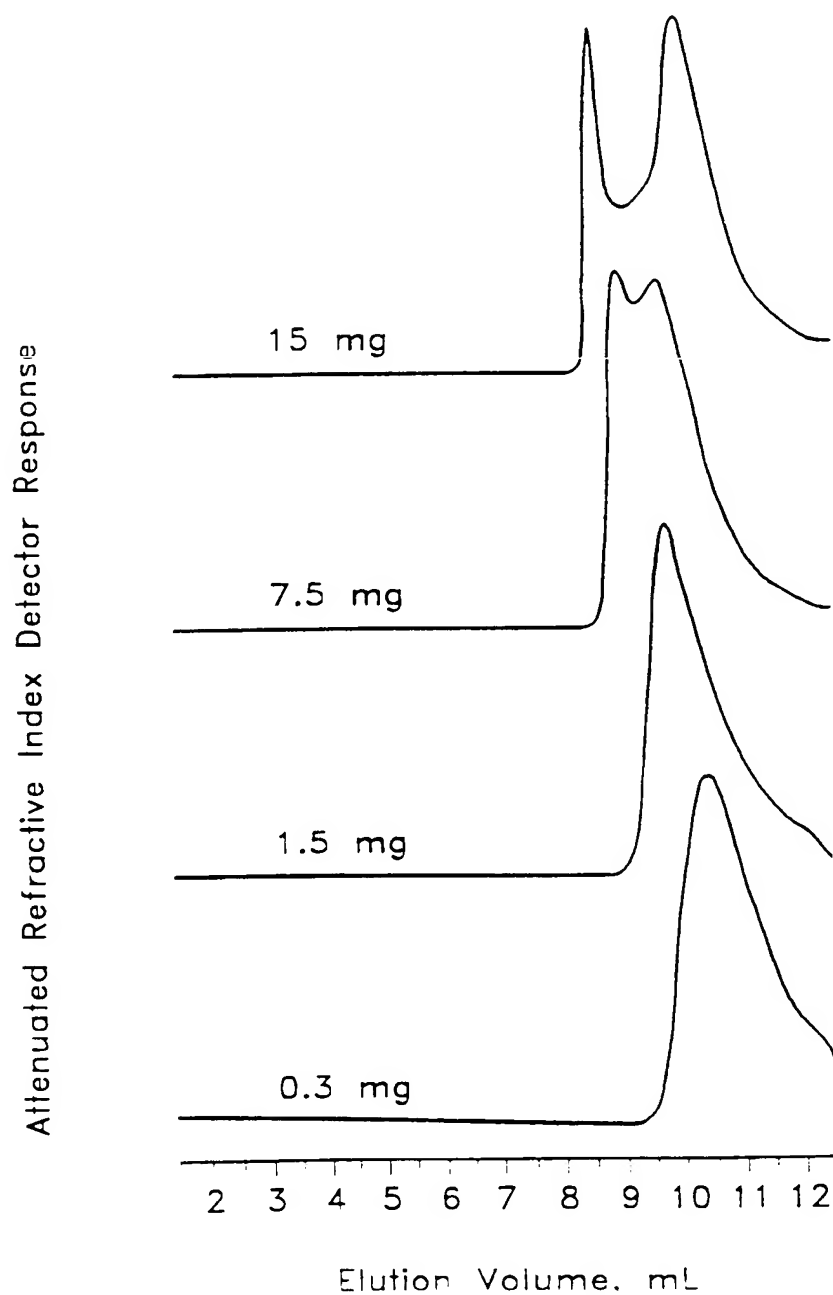


Fig. 5

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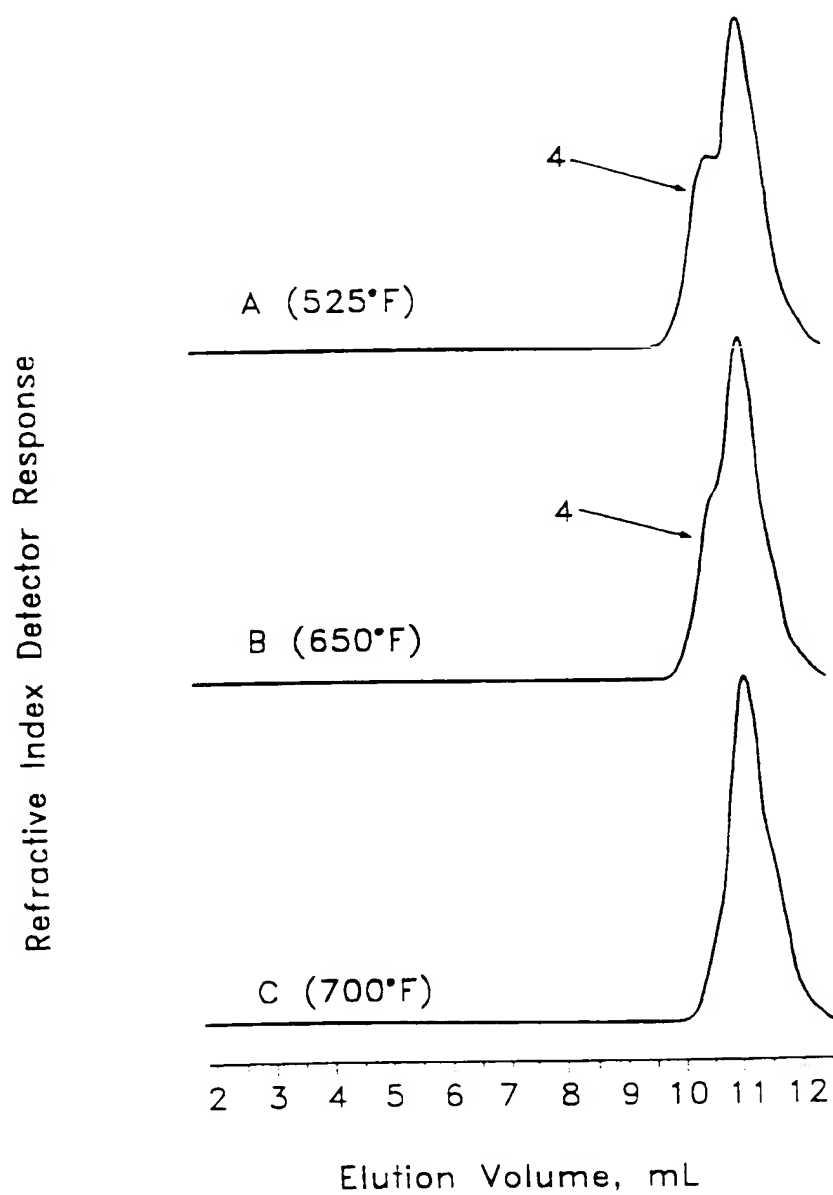


Fig. 6

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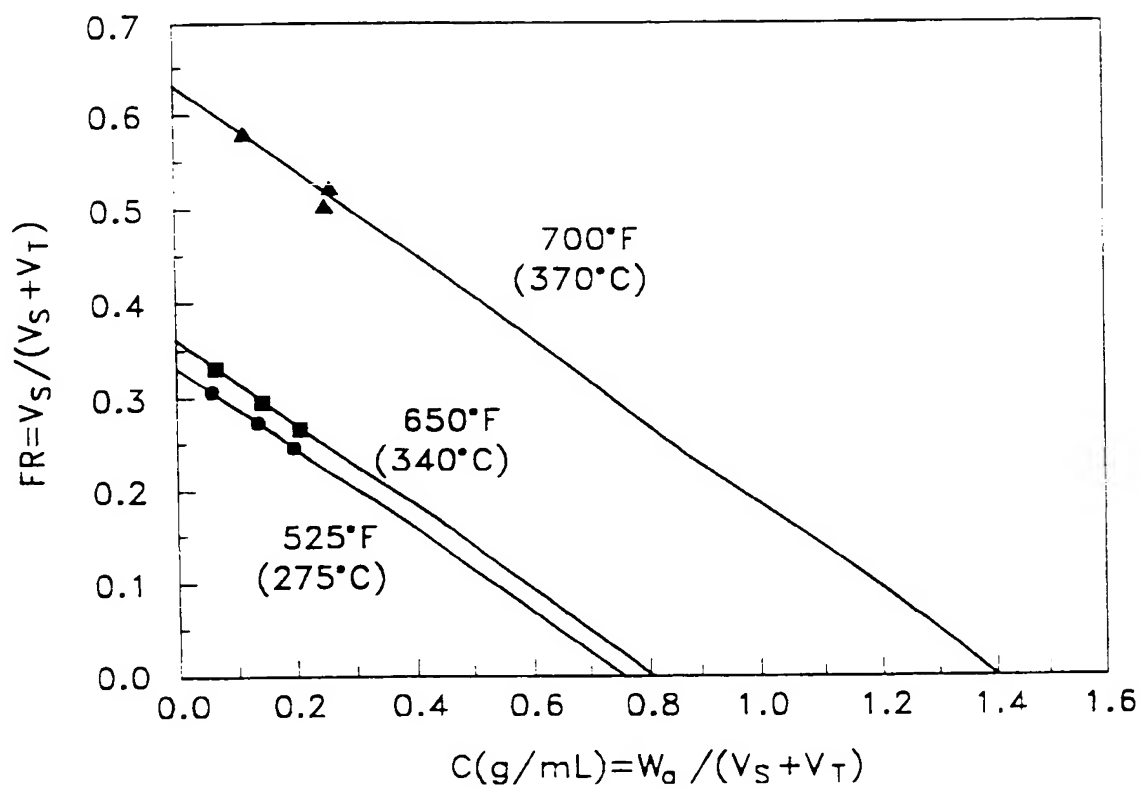


Fig. 7

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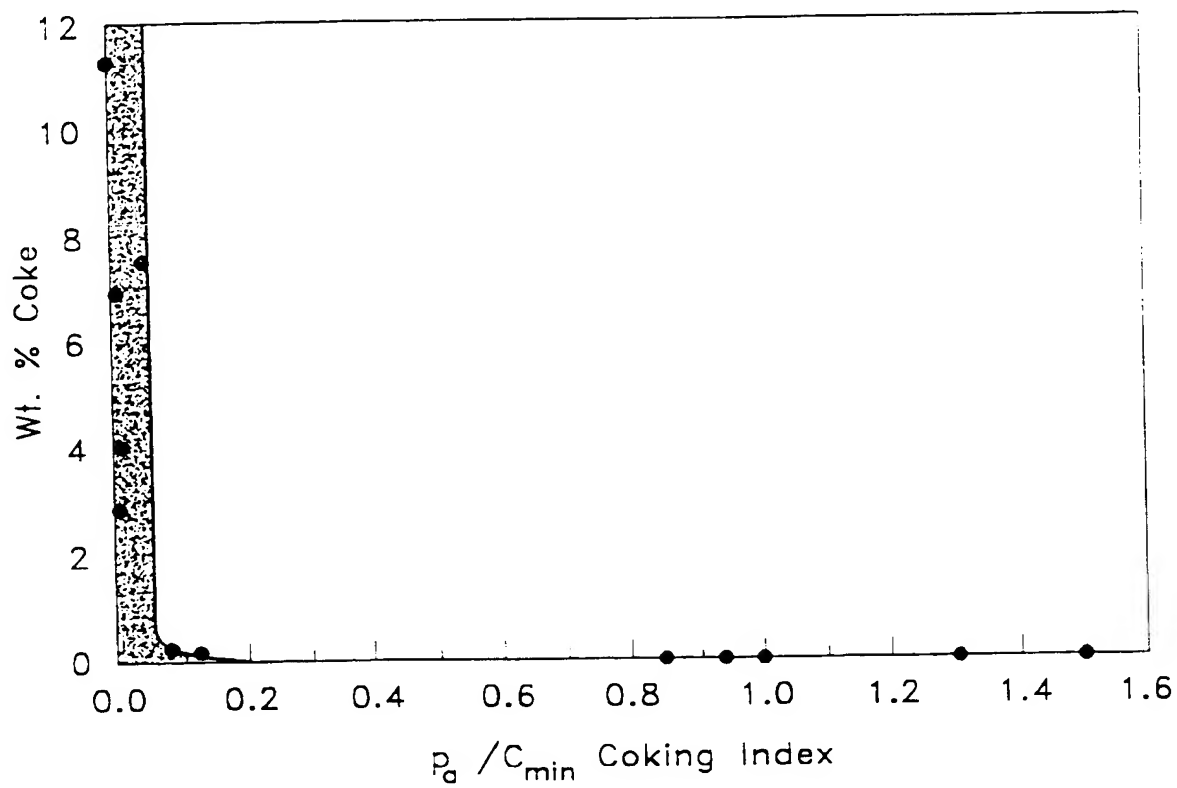


Fig. 8

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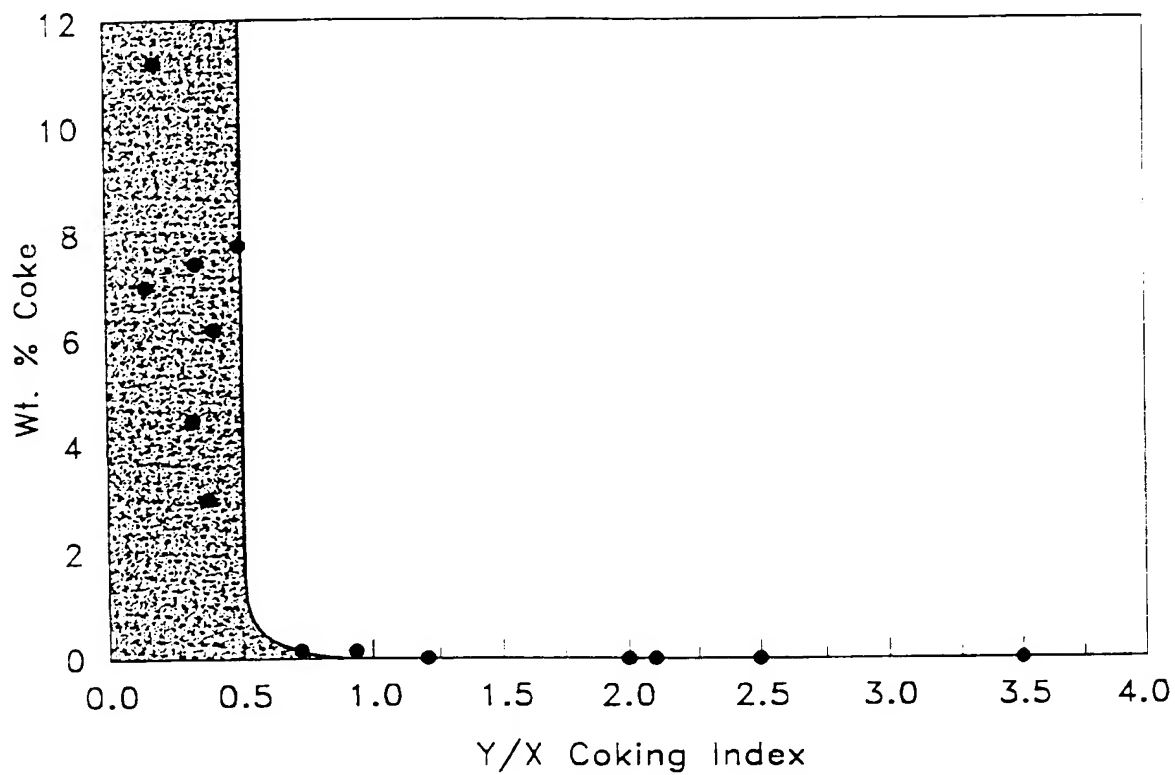


Fig. 9

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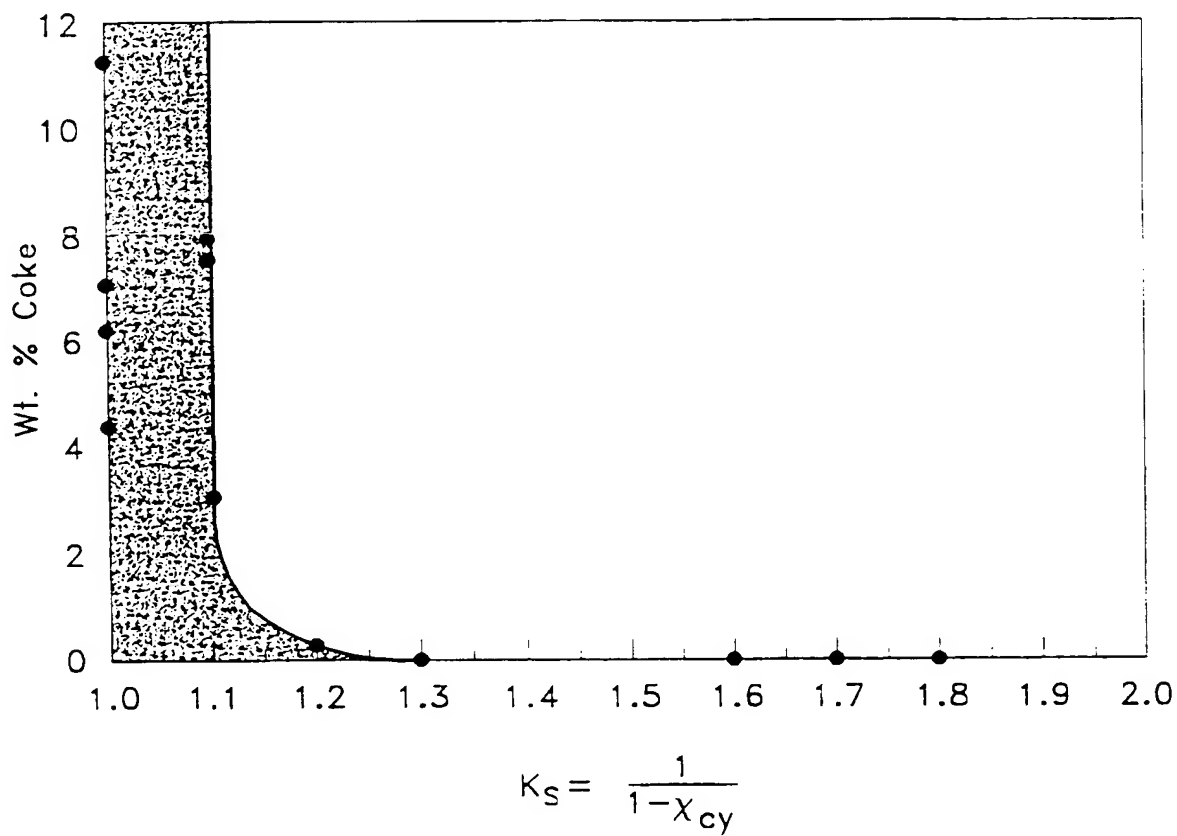


Fig. 10

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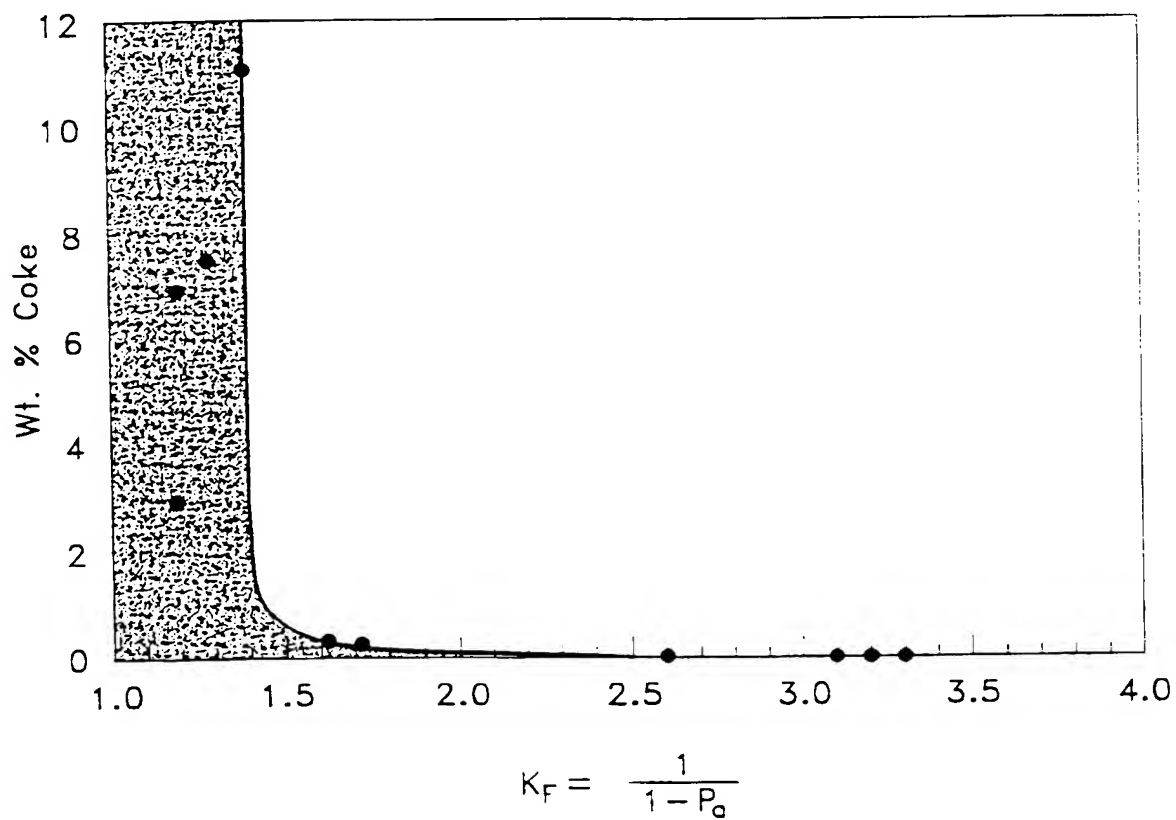


Fig. 11

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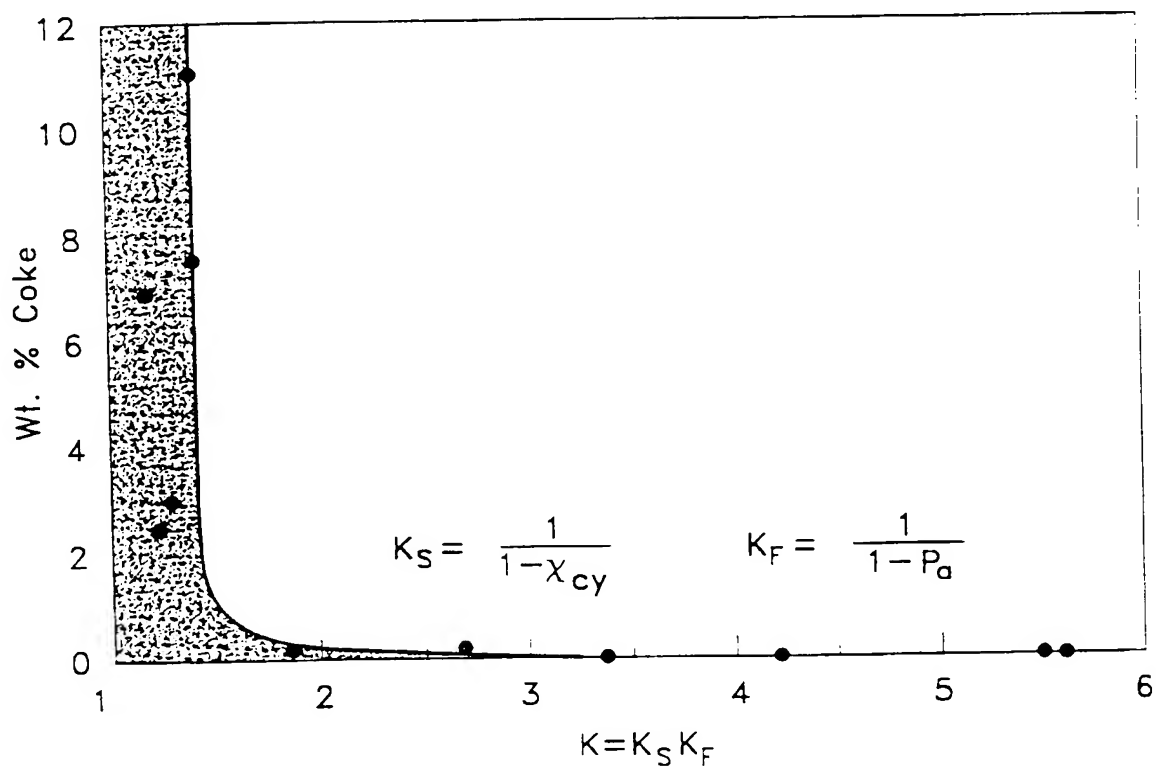


Fig. 12

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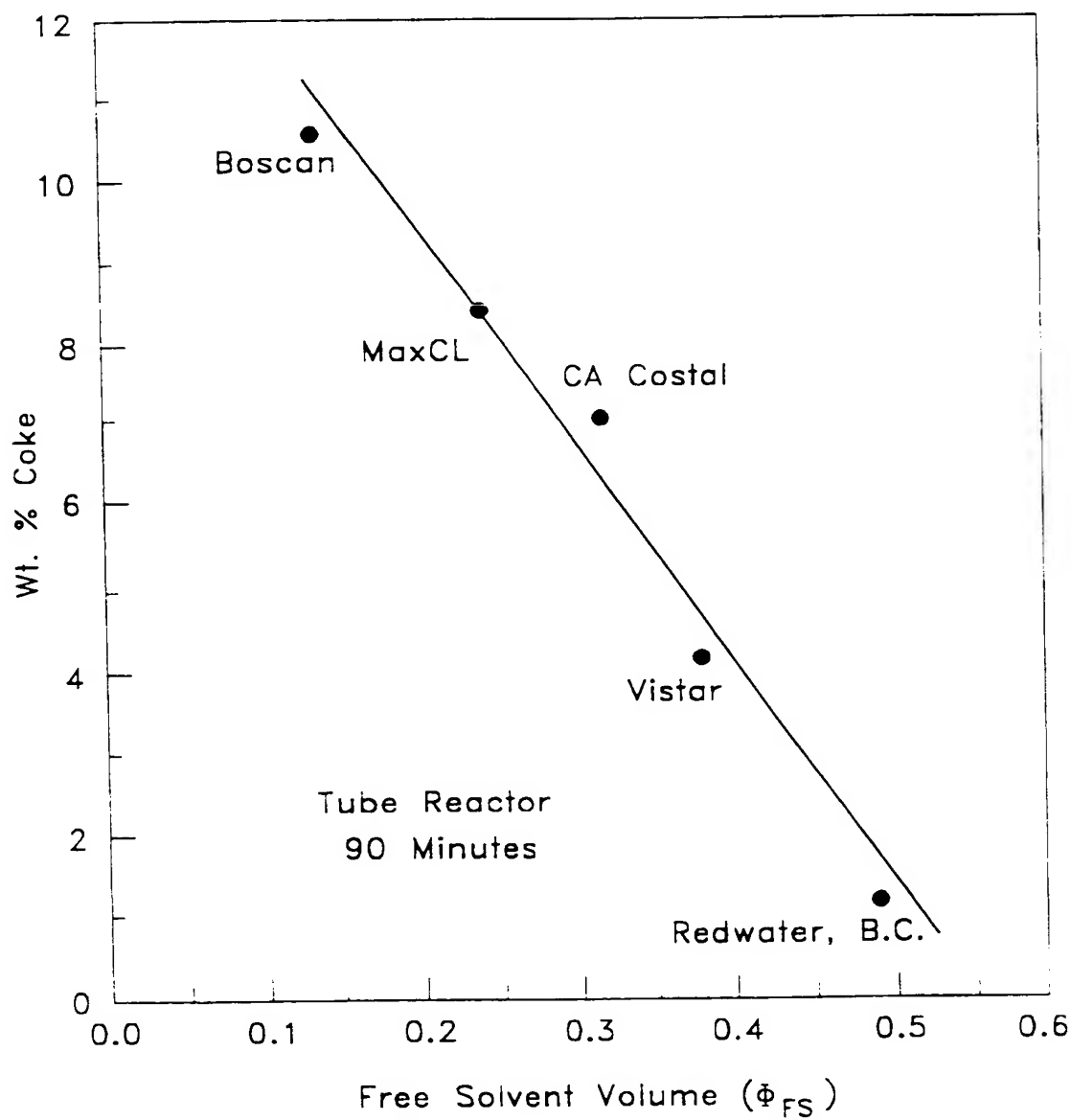


Fig. 13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/15950

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : GO1N 35/08, 31/00, 31/16, 33/00

US CL : 436/55, 60, 139, 163

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 436/55, 60, 139, 163

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,628,204 A (MAES) 09 December 1986, col. 1, 2, 4	17-26, 30-36, 45-49, 63-71, 79-89, 92, 93
Y	US 4,493,765 A (LONG ET AL.) 15 January 1985, Abstract, col. 1, lines 18-30,	37, 38, 50-56
Y	US 5,574,215 A (BUNGER ET AL.) 12 November 1996, Abstract, col. 10, lines 43-55	57-62
Y	US 5,092,983 A (EPPIG ET AL.) 03 March 1992, Abstract, col. 3 (A), (B), col. 4 (C)	50-58
Y	US 5,861,228 A (DESCALES ET AL.) January 19, 1999, Abstract, col. 1, lines 60-68, col. 2, lines 1-10	54-56



Further documents are listed in the continuation of Box C.



See patent family annex

*

Special categories of cited documents

T

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

A

document defining the general state of the art which is not considered to be of particular relevance

X

document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

E

earlier document published on or after the international filing date

Y

document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

L

document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O

document referring to an oral disclosure, use, exhibition or other means

Date

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/15950

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PAULI ET AL. Book of Abstracts, 217th ACS National Meeting, Anaheim, CA, March 21-25 (1999), PETR-007. American Chemical Society: Washington, D.C.	57-62

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/15950

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 1-16
because they relate to subject matter not required to be searched by this Authority, namely:

Rule 67.1. No International Preliminary Examining Authority shall be required to carry out an international preliminary examination on an international application if, and to the extent to which, its subject matter is any of the following: (v) mere presentations of information
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims, it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/15950

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

Group I, claim(s) 17-92, drawn to the method of processing a hydrocarbon material.
Group II, claim 93, drawn to the apparatus for processing the hydrocarbon material.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: method and apparatus of Groups I and II share the same technical feature which is well known in the art, namely any device from the group of NMR spectrometer, NMR tomograph, mass spectrometer, IR spectrometer, Raman spectrometer, gel electrophoretic or size exclusion or paper chromatograph.